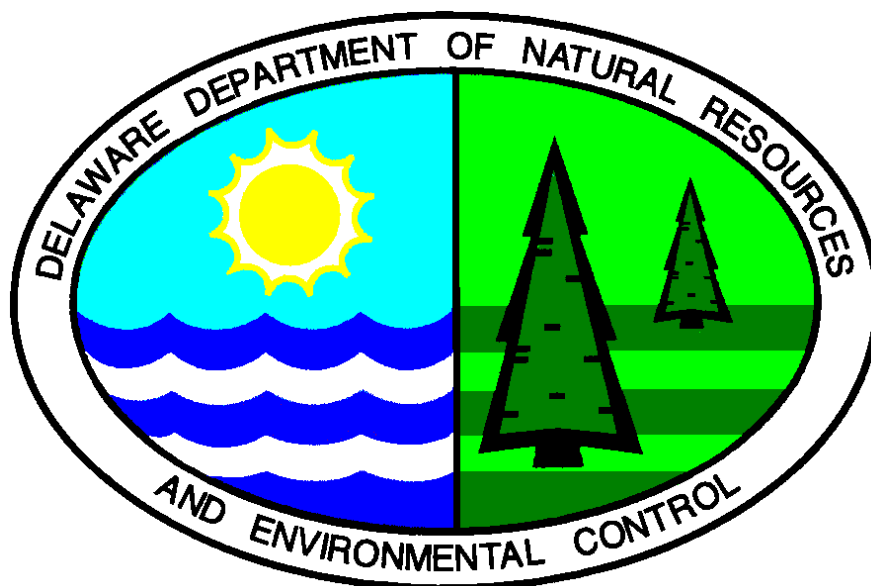


***DEPARTMENT OF NATURAL RESOURCES and  
ENVIRONMENTAL CONTROL  
SITE INVESTIGATION & RESTORATION BRANCH***



***STANDARD OPERATING PROCEDURES  
FOR  
CHEMICAL ANALYTICAL PROGRAMS  
UNDER THE  
HAZARDOUS SUBSTANCE CLEANUP ACT***

DNREC – SIRB QA Manager Approval: \_\_\_\_\_

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Appendix A Examples of Laboratory Forms

Appendix B Laboratory Audit Evaluation

## **1.0 INTRODUCTION**

### **1.1 Purpose**

The purpose of this document is to provide potentially responsible parties (PRPs) who are investigating hazardous waste sites under the provisions of the Delaware Hazardous Substance Cleanup Act (HSCA) with guidance on acceptable protocols for the chemical analysis of environmental samples. In most cases, the responsible party will contract with the laboratory providing analytical services for the cleanup project. However, the selection of the laboratory is subject to DNREC approval. A list of laboratories that are currently approved for HSCA projects is available from DNREC on request.

This document sets forth Quality Assurance (QA) program requirements for sampling and analysis projects undertaken to comply with DNREC HSCA corrective actions. The minimum quality requirements presented in this document are designed to ensure that sample collection and laboratory analysis activities generate data which meet DNREC project requirements, and are technically valid and legally defensible relative to the use for which the data are obtained.

Included in this document are the acceptable analytical method performance elements, a summary of minimum sample collection volumes, sample preservation requirements and maximum holding times, detailed requirements for analytical quality assurance and quality control and the necessary format for report deliverables. In addition, outlines of the procedures used by DNREC to identify qualified laboratories are included.

Minimum program requirements that are mandatory for DNREC analytical projects are specified throughout this document by the use of the terms “shall” or “must.” Information that is provided as guidance that constitutes an acceptable means of accomplishing a desired objective is designated by the terms “should” (recommended) or “may” (permissible).

### **1.2 Program Background**

This revision of *Standard Operating Procedures For Chemical Analytical Programs Under The Hazardous Substance Cleanup Act* (HSCA SOP CAP) represents a significant change in DNREC's approach. In the past, the HSCA SOP CAP required use of methods that were developed, promulgated and required by the USEPA. These methods do not always employ the best available instrument technology and/or analytical technique to meet project-specific data quality objectives (DQO) in a timely and cost-effective manner. In recognition of those potential shortcomings, DNREC now permits the use of performance-based methods, and this revision of the HSCA SOP CAP incorporates their use.

### **1.3 Performance Based Methods**

Performance based methods (PBM) are intended to provide the laboratory with more flexibility in meeting project requirements. The foundation of the PBM approach is establishment of performance criteria within which specified measurements must fall. The basic analytical approach is also specified. The laboratory is then permitted to use the specified analytical

approach in any manner it deems appropriate, so long as the specified performance measurements are made and fall within the specified criteria.

Performance criteria may come from any of the following sources, in order of precedence:

1. Project-specific documents
2. A reference method
3. This document

DNREC has the ultimate authority to determine analytical performance criteria for each project.

#### **1.4 Data Quality Objectives and Project Quality Assurance Plans**

Data quality objectives (DQOs) are qualitative and quantitative statements that specify the quality of the data required to support DNREC decisions during remedial response activities. DQOs are based on the intended end uses of the data, and may vary according to the needs of each project. Depending on the project phase, data may be collected to characterize a site, evaluate remedial alternatives, determine design criteria, or monitor site conditions and/or remedial action effectiveness. DQOs are applicable to all data collection activities, including those performed for preliminary assessments/site inspections (PA/SI), remedial investigations (RI), feasibility studies (FS), remedial design (RD), and remedial actions (RA).

For each DNREC project, a Project Quality Assurance Plan (PQAP)/Work Plan will be developed. The PQAP is a project-specific document that establishes the requirements for sampling and analysis necessary to ensure that DQOs are met. For each analysis required for the project, the Sampling and Analyses Plan (SAP) will contain detailed specifications regarding QC measurements required and the acceptance criteria for those measurements. **THE PQAP IS THE PRIMARY SOURCE OF ANALYTICAL QC REQUIREMENTS. QC SPECIFICATIONS IN THE SAP SUPERSEDE QC REQUIREMENTS IN THE ANALYTICAL METHOD AND IN THE LABORATORY'S SOP.**

Rather than listing specific QC measurements and criteria, the PQAP may cite the HSCA SOP CAP as the source of analytical QC specifications. If that is the case, the applicable specifications in Section 6 of this document are to be used.

#### **1.5 Reference Methods**

Reference methods are another potential source of performance criteria. A reference method (see Section 5 of this document for a list of reference methods) is a published EPA method that may include required QC measurements and acceptance criteria for each measurement. The current EPA Contract Laboratory Program Statement of Work for Volatile Organics is an example of a reference document.

Reference methods may be included in the PQAP for a DNREC project in one of two ways:

1. The PQAP may call for the use of the reference method for the required analysis<sup>1</sup>
2. The PQAP may cite a reference method as the source of performance measurements and acceptance criteria, without specifying the use of the method.<sup>2</sup>

Figure 1.1 shows the hierarchy for selection of analytical methods and performance criteria under DNREC's performance based method system.

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<sup>1</sup> Although DNREC permits the use of performance based methods, they are not required. Project personnel can specify the use of a specific method in the PQAP, in which case the laboratory is required to use the specified method.

<sup>2</sup> In this case, the laboratory is free to choose any appropriate analytical method, but must ensure that it meets the performance criteria in the reference method cited in the PQAP.

## **2.0 LABORATORY EVALUATION**

Laboratories that perform analytical work in conjunction with DNREC projects must successfully complete the evaluation process described in this document prior to initiating analysis of samples. This section describes the elements involved in the evaluation process used to initially qualify laboratories to perform analytical work and the ongoing requirements to maintain the DNREC approval status. The evaluation process outlined here applies to the majority of analytical projects falling under DNREC oversight. However, unique analytical protocols (e.g., dioxin, radiochemistry, etc.) required in certain project-specific plans will involve additional evaluation elements as determined by DNREC.

### **2.1 Responsibility of the PRP**

It is the PRP's responsibility to propose each individual subcontract laboratory for the project analytical work and to serve as the liaison between the proposed laboratory(ies) and DNREC evaluation personnel to ensure that all necessary qualifications documentation is submitted in a timely fashion to complete the evaluation process prior to the receipt of project samples. Once the laboratory successfully completes the evaluation process and is approved for DNREC analytical work, the PRP (or its consultant) will make all arrangements with the laboratory concerning contractual obligations, project schedules, bottle orders, sample shipments from the field and reporting of data in the appropriate format for submittal to DNREC. Ordinarily, DNREC will not communicate directly with the laboratory.

The PRP must submit the name, address, phone number and point of contact (i.e., Laboratory Project Manager) for its proposed subcontract laboratory(ies) to DNREC. DNREC requires that the designated point of contact work within the physical location of the proposed laboratory, rather than from an affiliated marketing or corporate office. Based on the DNREC requirement that all analyses associated with a project be performed by an approved laboratory, any laboratory which will require subcontracts to satisfy project scopes of work must identify all proposed second tier subcontract laboratories, so that those laboratories may be evaluated. This requirement also applies to affiliated "network" laboratories in separate locations that may operate under a single corporate QA plan.

### **2.2 DNREC Oversight**

As the enforcement agency whose decisions regarding litigation, cleanup requirements, and human health and environmental risks are based largely on laboratory generated data, DNREC will actively oversee the selection of the laboratory and its analytical procedures. DNREC reserves the right to split samples for analysis by a different laboratory to ensure consistency and quality.

### **2.3 Laboratory Evaluation and Qualification**

Prior to participation in a DNREC project, the analytical laboratory must be evaluated to determine its physical and operational capabilities to provide the desired analytical support. Based on project-specific requirements, the evaluation process can vary from a standardized review of a laboratory's execution of standard methods (see the copy of the DNREC laboratory

audit evaluation checklist in Appendix 1) to one that verifies adequate execution of performance-based methods. The proposed laboratory is required to demonstrate and document its ability to meet the project criteria and to produce the specified deliverables.

### **2.3.1 Initial Evaluation**

The laboratory approval process starts with a documentation review. The purpose of this review is to assess current physical operations, staff experience and quality systems, and past performance on performance evaluation studies relevant to the analyses included in the proposed project. Specifically, DNREC requires that a prospective laboratory submit:

1. a copy of any relevant Quality Assurance (QA) Manuals applicable to proposed project-specific analytical protocol;
2. a copy of a Statement of Qualifications (SOQ) or similar facsimile document covering the information outlined in Section 2.3.1.2; and
3. copies of the results (including corrective actions, as appropriate) from Performance Evaluation conducted and/or required by federal/state agencies during the last two years.

The documentation will be reviewed by DNREC to determine if the laboratory has the appropriate instrumentation, personnel, training, capacity, and programs for quality and safety to meet the needs of the proposed project.

If the QA Manual and SOQ indicate that adequate programs are in place at the laboratory and that further consideration is warranted, DNREC will evaluate the laboratory's ability to perform the desired analyses through assessment of Performance Evaluation (PE) sample scores. After the PE sample results have been evaluated, DNREC will conduct an on-site audit of the laboratory facility. The PE sample results will be discussed at this time, including discrepancies and possible corrective actions. This is an important opportunity for the laboratory to present explanations for why some PE results may not have met specifications and to initiate appropriate corrective actions that may prevent disqualification by DNREC.

#### **2.3.1.1 *Quality Assurance (QA) Manual***

The laboratory's formal and comprehensive Quality Assurance Manual must be provided to the DNREC as part of the initial qualification process. At a minimum this document must include clear documentation of routine procedures for:

- sample container procurement, preparation, and verification procedures to document the absence of contaminants;
- preparation of contaminant-free water and soil to provide matrix-specific blanks for the samples being collected;
- Chain-of-custody procedures, beginning with the preparation or procurement of sample containers through all processes associated with sample receipt, analytical processing, and disposal;
- document control and review procedures, beginning with generation of raw data and ending with archival of final reports;
- sample receipt, storage, and handling;

- quality control, including laboratory blanks, duplicates, replicates, spikes, screening, and re-extractions/reanalyses;
- performing all methods routinely employed by the laboratory, including a list of methods (by EPA or other Method reference as appropriate) performed by the laboratory, with applicable matrices specified;
- documenting performance comparability to a reference method for all performance-based methods employed by the laboratory;
- listing of titles of the laboratory's currently approved Standard Operating Procedures (with SOP number, revision number, and date of approval);
- data quality assessment and corrective action;
- data assembly, report generation (hardcopy and diskette), report distribution, and data archival; and
- sample/extract/digestate disposal.

Based on its reviews and audits, DNREC will notify the proposed laboratory in writing of any deficiencies or concerns that may preclude the laboratory from meeting analytical requirements and DQOs for the specific project. The laboratory is required to address and resolve each of the deficiencies/concerns identified by DNREC. In most cases, this will require revision of the QA document(s).

### ***2.3.1.2 Statement of Qualifications (SOQ)***

The laboratory's Statement of Qualifications must be provided to the DNREC for review as part of the initial qualification process. At a minimum this document must include:

- A general description of the size and location of the facility. This document may include other divisions if a network exists although the specific location must be unequivocally identified and only the laboratory under evaluation will be considered.
- A listing of major instrumentation routinely available for production analyses. The list must address only the facility under evaluation. The information must include the manufacturer, model number, year acquired, service arrangements (service contract or in-house repairs), and predominant use of the instrument.
- An organizational chart of key personnel that includes name, title, and department. The chart must accurately represent the routine flow of responsibility in the laboratory.
- Job description for key personnel positions.
- Resumes for all personnel that will participate on DNREC projects.
- A signature sheet of all personnel listing printed name, signature, and signed initials. (Please Note: In lieu of having this information in the SQO, each laboratory department must have this information documented for review during an on-site audit.)
- An itemization of prior (five years) experience divided into two sections: (1) Government Contracts and (2) Private Sector/Industrial Clients. This information must include the client, client contact and telephone number, the contract number (or purchase order number), the value of the contract, the contract initiation and termination date, and a general description of the project. If performance evaluation samples were required by a contract, all associated evaluation results must be reported in terms of satisfactory or unsatisfactory performance. (Please note: In lieu of having this information in the SQO, the laboratory may present this information at the time of an on-site audit).

- A list of reference contacts including the client name, company, address, and phone number (Please Note: In lieu of having this information in the SQO, the laboratory may present this information at the time of the on-site audit).

If appropriate, some of this required information may be provided in the laboratory QA manual (such as inclusion in appendices that can be revised as needed).

### ***2.3.1.3 Performance Evaluation***

The proposed laboratory's ability to successfully complete proficiency testing through the analysis of PE samples is a critical component of the laboratory evaluation process. For PE results to be deemed appropriate for assessment by DNREC, the proficiency testing must be for an analytical method and sample matrix similar to the project-specific analytical services to be provided by the proposed laboratory. If the laboratory is participating in programs that include regular monitoring of performance, DNREC may opt to review the most recent performance evaluation results under the other programs to evaluate the laboratory. If the laboratory is not participating in any programs with routine performance checks, DNREC may procure and submit its own Performance Evaluation (PE) samples to the candidate laboratory.

The laboratory is required to analyze the PE samples using the methods and procedures to be used to perform DNREC project work. The laboratory must clearly document and report the method(s) used for analysis of PE samples, including as appropriate: EPA method number and version; laboratory-specific performance-based method name and revision; and internal SOP number and version. DNREC may require that the results of these analyses be submitted in a data package similar to that desired for a specific project so that the ability to report results completely and accurately may also be assessed. The type of report desired will be defined prior to acceptance of the PE samples by the laboratory. At the discretion of DNREC, laboratories that do not generate acceptable results for the PE samples may not be considered further.

### ***2.3.1.4 On-site Laboratory Audit***

Once the laboratory's documentation has been reviewed and found to be adequate, DNREC will conduct an on-site operation and quality systems audit. This is the final element in determining the suitability of the proposed laboratory to perform analytical services for DNREC projects. The audit will verify the laboratory's facility and analytical instrumentation inventory, QA/QC policies, operational practices, and technical documentation relative to:

- Requirements set forth in this document, unless superceded by project-specific requirements;
- Reference method requirements and/or technical justification of performance-based method procedures;
- Requirements described in the laboratory's QA documentation and SOPs;
- Facility layout and instrumentation as specified in the SQO; and
- Good laboratory practices (GLP) and good automated laboratory practices (GALP).

The scope of the audit will be based on project-specific requirements. This will involve the evaluation of the laboratory's comprehensive quality assurance (QA) management procedures and controls and the operational quality control (QC) practices used to generate data of

acceptable quality relative to project DQOs. All aspects of routine laboratory operations that can potentially impact on project performance will be reviewed, including:

- sample bottle preparation and shipment,
- sample login and storage,
- workflow management (i.e., Laboratory Information Management System – LIMS),
- sample preparation and analysis,
- quality control applications,
- data processing and review,
- reporting of results, and
- data storage.

In addition, documentation of the effectiveness of the laboratory's QA program and corrective action system will be assessed, adherence to SOPs will be documented, method startup and analyst's initial demonstration of method performance documentation will be reviewed, and the systems and practices for data reduction, integrity, review and reporting will be evaluated. Audit trails of generation, reporting and archiving of data will be reviewed to verify the ability to easily recreate and legally defend the result reported. The facility layout, staff experience, equipment inventory, administrative systems, management organization and corporate structure will be verified. A standardized laboratory audit checklist can be found in Appendix 1.

DNREC will issue an audit report detailing deficiencies noted during the on-site assessment. The laboratory will respond in writing with a proposed corrective action plan to bring the laboratory operation into compliance with DNREC program requirements. Failure to correct deficiencies cited will preclude approval of the proposed laboratory to perform analytical services in conjunction with DNREC projects.

Once a laboratory has been approved to participate in a DNREC HSCA project, the laboratory will be added to DNREC's Approved Laboratory list. This qualifies the laboratory to participate in other DNREC HSCA projects.

### **2.3.2 On-Going Evaluations**

Laboratory evaluation will continue on a regular basis for the duration of each project to ensure that the quality of the analytical data generated does not deteriorate over time. Laboratories participating in DNREC HSCA projects will be required to analyze performance evaluation (PE) samples at a frequency determined by DNREC.

PE samples may be analyzed immediately prior to analyses of actual field samples or during the analyses of the initial samples from the field.

- DNREC may periodically procure and submit, or require PRPs to procure and submit, PE samples to laboratories conducting analyses for a specific project. The PE samples can be obtained from vendors for most parameters and matrices. The PE samples will be transferred to sample containers and submitted to the laboratory identified only as typical field samples. Results of the PE sample analyses will be reported with the field sample results.

- Performance evaluations completed for another agency such as the US EPA may be considered by DNREC in lieu of requiring additional PE's. This decision will be made on a case-by-case basis and assumes attainment of a satisfactory score in the alternate PE.
- If PE sample analyses are conducted by the PRPs, they will be conducted at not cost to DNREC. Written notification of failure to successfully perform PE sample analyses must be forwarded to DNREC within twenty-four (24) hours. Furthermore, failure of the laboratory to successfully perform PE sample analyses conducted under programs not associated with DNREC projects must be reported to the DNREC within twenty-four (24) hours of receipt of the notification by the laboratory.
- Announced or unannounced laboratory audits may also be conducted during the performance of project work. The laboratory may be required to demonstrate their procedures for proper storage and handling of samples and to provide all project data and related documentation generated to date (including laboratory notebooks, preparation/extraction logs, weight log, pH logs, run logs, instrument maintenance logs, project file folders and internal chain of custody records) for review. In addition, the laboratory may be required to allow DNREC access to tuning, calibration, and/or blank data associated with the project. DNREC may also evaluate the laboratory's safety, record keeping, and housekeeping procedures.

### **2.3.3 List of Approved Laboratories**

DNREC will maintain a list of laboratories that have successfully completed the evaluation process and are, therefore, deemed capable of providing analytical support. This list will be reviewed and revised periodically. New laboratories may be added, and some laboratories may be deleted depending on the results of recent evaluations. A periodic review is essential to ensure that laboratories on the list at any given time are known to be maintaining acceptable quality standards. A current list of DNREC approved laboratories can be found at <http://sirb.awm.dnrec.state.de.us/labs.htm>

Evaluation of laboratories is, of necessity, an on-going process. The regular introduction of new analytical methods, the continued advancement of instrumentation, and the relatively high turnover of personnel typical in environmental analytical laboratories result in even the best facilities being in a constant state of change. Therefore, for a laboratory to remain on the List of Approved Laboratories, at the sole discretion of DNREC, it will be subject to periodic audits even if not actively engaged in a DNREC HSCA project.

## **2.4 Analytical Project Management**

The single most important aspect of analytical project management is communication with the laboratory to ensure that the project requirements are understood. Complete and clear communication must be initiated before any site work is begun and must be maintained for the duration of the project. The DNREC Project Officer is responsible for ensuring that the necessary communications with the laboratory are initiated and maintained regardless of whether the laboratory is directly under contract with DNREC or a PRP.

### **2.4.1 Responsibilities of the PRP**

The PRP is responsible for ensuring that all analytical requirements are documented and understood by the laboratory. The vehicle for documenting the analytical requirements is the Project Quality Assurance Plan (PQAP). The PRP may choose to employ the services of a

consultant to assist in fulfilling the PRP's responsibilities. If this is the case, the consultant must be approved by DNREC. A description of required qualifications for consultants can be found at the DNREC web site at <http://sirb.awm.dnrec.state.de.us.consult.htm>. A link to the current list of approved consultants can also be found at that address.

#### **2.4.2 Initial Laboratory Contact**

An Analytical Services Solicitation Form (Figure 2-2) is useful in tabulating project requirements and associated cost estimates. The sponsoring organization (DNREC or PRP) would be responsible for completing most of the information requested on the form. The cost column should be left blank and should be completed by the laboratory proposing to conduct the chemical analyses for the project. Definition of the project requirements by the DNREC Project Officer (or a PRP) will be reflected in the information provided on the Analytical Services Solicitation Form, and the form may serve as a guide in reminding the project officer of the information required by the laboratory.

#### **2.4.3 Ongoing Laboratory Communication**

Each sampling site is unique and may require specialized attention to project-specific details in order to best meet the established data quality objectives. Frequent contact between DNREC (or PRP) and the laboratory must be maintained throughout the project. The frequency of the contacts will be dependent on the problems encountered and/or the criticality of the stage of the project. Awareness of the status of the project at the laboratory must be maintained at all times, and appropriate guidance must be given to the laboratory in a timely manner.

Most communication with a laboratory may be handled in a telephone conversation but must always be followed up with written documentation. In instances where the phone conversation involves only an exchange of information that does not impact on project performance, requirements, or objectives, a written phone log of the conversation will suffice. When problems are discussed, decisions are made, or areas of concern require attention, a letter must be mailed or faxed documenting the conversation and the desired course of action. The written document must be transmitted from the originator to affected parties within 24 hours. The document originator will normally be the party that will be required to effect an action to ensure that the required action is fully understood. The party required to document the discussion will be identified and agreed upon during the conversation.

#### **2.4.4 Analytical Laboratories**

The laboratory will usually provide a customer service liaison (laboratory project manager) for each project as a point of contact for the PRP's project manager. This individual should be able to advise the project manager on logistical matters and on the status of the analytical work at all times. The Quality Assurance/Quality Control (QA/QC) Officer for the laboratory does not report directly to the Laboratory Project Manager. This is intentional and serves to minimize the potential sacrifice of data quality to achieve production and/or budgetary goals. The organizational structure also encourages active participation in the analytical process by the QA/QC Officer, especially with respect to problem solving.

#### ***2.4.4.1 Key Laboratory Personnel***

There are at least four (4) key roles that must be identified within the laboratory for each DNREC project that is undertaken: 1) the Project Director; 2) the Project Manager; 3) the QA/QC Officer; and 4) the Manager of each applicable department. The number of additional supporting personnel involved in project analyses will depend on the magnitude and nature of the particular project.

##### **2.4.4.1.1 Project Director**

The individual serving in the role of Project Director will perform the following functions:

- responsible for all contractual obligations of the project,
- reviews technical performance,
- reviews schedules,
- monitors costs,
- redirects work efforts as necessary to achieve project objectives, and
- provides an independent avenue of communication for the DNREC Project Manager.

##### **2.4.4.1.2 Laboratory Project Manager**

The individual serving in the role of Laboratory Project Manager will perform the following functions:

- answers directly to the Laboratory Project Director,
- serves as the primary contact for the DNREC Project Manager,
- responsible for the day-to-day management of the project staff,
- responsible for maintaining technical performance,
- approves and monitors all analytical and quality assurance/quality control (QA/QC) procedures, and
- responsible for meeting budgetary requirements.

##### **2.4.4.1.3 Laboratory QA/QC Officer**

The individual serving in the role of Laboratory QA/QC Officer will perform the following functions:

- answers directly to the Laboratory Project Director,
- responsible for monitoring technical performance, Responsible for implementing or approving corrective action when warranted, and
- assesses data quality based on professional judgment and method compliance prior to release of the final report. See section 9.1.5 for specific quality review functions.

##### **2.4.4.1.4 Laboratory Department Managers**

The individual serving in the role of Laboratory Department Manager will perform the following functions:

- responsible for the technical aspects of each task associated with analyses in their department,
- serves as the principal investigator for each task, and

- supervises the activities of each member of the department.

## **2.5 Project Quality Assurance Plan**

On selection to participate in a DNREC project, the laboratory may assist the PRP or their designee in the preparation of a Project Quality Assurance Plan (PQAP) to delineate the specific laboratory procedures to be used. The project PQAP will encompass the relevant laboratory requirements as itemized in this and other sections of this document and will be discussed in sufficient detail that personnel previously unfamiliar with the project will easily comprehend the project-specific procedures.

### **2.5.1 Analytical Subcontractors**

Subcontracting analytical work from a specific laboratory approved by the DNREC for a given project, even to another previously approved DNREC laboratory or network laboratory, will be prohibited without prior written approval from the DNREC Project Manager.

## ***3.0 GENERAL LABORATORY PRACTICES***

This section describes the general practices required of laboratories performing work under the DNREC HSCA CAP.

### **3.1 Laboratory Organization and Personnel**

Laboratories performing work under the DNREC HSCA SOP CAP must have clearly defined corporate- and facility-specific operational hierarchy and lines of authority. Typically this information is included in the laboratory QA manual in the form of an organizational diagram or chart illustrating lines of authority and reporting responsibilities.

An effective organizational structure places direct and ultimate responsibility for assuring data quality with line management (e.g., chief executive officer, laboratory director, department supervisor), not the QA officer of the laboratory. The role of the QA function is to provide technical support to management for review and assurance of data quality. To prevent the over emphasis of production at the expense of data quality, every effort should be made to create independent lines of authority and reporting routes for QA functions.

A significant element of the DNREC laboratory assessment process is the evaluation of staff experience and capabilities to verify the operation's ability to meet project-specific requirements. Any significant changes in the laboratory organization and personnel must be reported to DNREC. Such changes may include facility mergers or acquisitions, laboratory expansions or moves, management reorganizations, and changes in primary technical or QA personnel. Regulatory actions toward the laboratory or its parent corporation, such as suspension of approval or contracts with federal and state agencies, as well as all notices of investigations and legal actions against the organization or its personnel must be reported immediately.

#### **3.1.1 Personnel Qualification**

The quality of data generated by a laboratory is largely dependent on the qualifications and capabilities of its personnel. Facilities and instrumentation are important but only experienced and qualified personnel can ensure the consistent production of high quality, reliable results. The availability of a sufficient number of qualified staff members to handle all stages of sample processing is essential. In order to ensure continuous operations to accomplish the required work, redundancy in key positions is essential. The maintenance of schedules must not be dependent on a single individual.

In evaluating laboratory capabilities, DNREC places special emphasis on the value of actual hands-on laboratory experience. In gauging an analyst's ability to generate data of known quality and usability, years of analytical experience can be the over riding factor when compared solely to academic achievement. The laboratory must have an internal analyst proficiency evaluation policy that defines a formal process to assess and document the competence of experienced individuals, as well as specifying additional training and documentation practices applicable to all personnel. Laboratory staff that have not been trained and evaluated shall not be utilized in the handling or analysis of DNREC project samples.

The laboratory must maintain comprehensive information on each laboratory staff member concerning the individual's formal education, training and laboratory experience. This should include such documentation as copies of the individual's up-to-date resume, degrees earned, certificates of analytical instrumentation training courses completed, and records of in-house training. In addition, documentation of "initial demonstration of proficiency" for analytical methods performed by the individual must be included.

### **3.1.2 Training**

It is the responsibility of the line manager/supervisor to ensure that laboratory staff under their direction have the needed education, training and experience to produce quality work. Laboratory staff must receive training commensurate with their experience and responsibilities. All pertinent training should be documented through attendance records of in-house training, individual instruction verified through the instructor's signature, or certificate, and sign-off sheets acknowledging the reading and understanding of relevant standard operating procedures documents.

#### ***3.1.2.1 Initial Demonstration of Analyst Proficiency***

The laboratory must establish and implement a policy that requires the initial demonstration of analyst proficiency in the methods or procedures they perform. This is of particular concern when the laboratory uses performance-based methods. Each laboratory technician or analyst that prepares or analyses samples must demonstrate their ability to successfully execute each method. to qualify to perform a given analytical method, the individual must, at a minimum, successfully process an independently prepared single blind proficiency sample. For any performance-based and all organic analytical methods, demonstration of accuracy and precision using analysis of quadruplicate samples is required. The demonstration must be performed without direction and should be completed following the documented training in the analytical protocol. Acceptance criteria for successful performance must be defined in the applicable analytical SOP and be consistent with the requirements of the reference method. Compliance with method LCS acceptance criteria, as long as the criteria are at least as rigorous as those specified in the reference method, is considered acceptable. Compliance with acceptance limits developed from peer group performance (as provided with commercially available PE samples) is also considered acceptable.

### **3.1.3 Personnel Requirements**

DNREC projects typically require analytical work for the qualitative and quantitative assessment of contaminants comprising the Target Analyte List (TAL) for inorganic analytes and Target Compound List (TCL) for organics. To meet the minimum TAL/TCL analytical requirements of DNREC projects the approved laboratory must have experienced staff in a minimum of 16 critical roles or positions. Per Section 3.1.2, the relevant analytical experience of all staff must be documented in their individual training records.

Minimum recommended qualifications for laboratory personnel in key positions are listed below. The following are recommendations only. A laboratory's capability for meeting the data quality requirements must be demonstrated as stated otherwise herein, regardless of personnel qualifications.

Laboratory Project Director	BS degree in chemistry or any scientific/engineering discipline and five years of laboratory experience, including at least three years of supervisory experience.
Laboratory Project Manager	BS degree in chemistry or any scientific/engineering discipline and three years of laboratory experience, including at least one year of supervisory experience.
Laboratory Quality Assurance/Quality Control Officer	BS degree in chemistry or any scientific/engineering discipline and three years of laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory.
GC/MS Laboratory Supervisor	BS degree in chemistry or any scientific/engineering discipline and three years of experience in operating and maintaining GC/MS/DS instrumentation, including at least one year of supervisory experience.
GC/MS Operator	BS degree in chemistry or any scientific/engineering discipline and one year of experience in operating and maintaining GC/MS/DS <u>or</u> three years of experience in operating and maintaining GC/MS/DS instrumentation.
Mass Spectral Interpretation Specialist	BS degree in chemistry or any scientific/engineering discipline, training course(s) in mass spectral interpretation, and two years of experience in this area.
GC Laboratory Supervisor	BS degree in chemistry or any scientific/engineering discipline and three years of experience in operating and maintaining GC instrumentation and interpreting GC chromatograms, including at least one year of supervisory experience.
GC Operator	BS degree in chemistry or any scientific/engineering discipline and one year of experience in operating and maintaining GC instruments or three years of experience in operating and maintaining the GC instruments and interpreting the GC data.
Sample Preparation Laboratory Supervisor	BS degree in any scientific/engineering discipline and three years of environmental laboratory experience, including at least one year of environmental laboratory experience, and three years of experience in preparation/cleanup of environmental samples for organic analysis, including at least one year of environmental supervisory experience.
Extraction/Concentration Technician	high school diploma and a college level course in general chemistry with one year of experience in extraction/concentration.
Inorganic Laboratory Supervisor	BS degree in chemistry or any scientific/engineering discipline and three years of laboratory experience, including at least one year in a supervisory position.
ICP or ICP-MS Operator	BS degree in chemistry or any scientific/engineering discipline, specialized training in ICP spectroscopy or ICP-MS spectrometry, and one year of applied experience with ICP or ICP-MS analysis of environmental samples or, in lieu of the educational requirement, three or more years of experience in operating and maintaining ICP or ICP-MS

	instrumentation.
Atomic Absorption Spectrometer (AAS) Operator	BS degree in chemistry or any scientific/engineering discipline with one year of experience in operating and maintaining AA instrumentation for graphite furnace, flame, and/or cold vapor AA or, in lieu of the educational requirement, three or more years of experience in operating and maintaining AA instrumentation, including graphite furnace, flame, and cold vapor techniques.
Inorganic Sample Preparations Specialist	high school diploma and a college level course in general chemistry or equivalent and one year of experience in sample preparation in an analytical laboratory. If microwave digestion is used there must be six months experience in an analytical laboratory and six months experience in sample dissolution using microwave digestion techniques.
Classical Techniques (Wet Chemistry) Analyst	BS degree in chemistry or any scientific/engineering discipline and one year of experience with classical chemistry laboratory procedures, in conjunction with the educational qualification or, in lieu of the educational requirement, two years of experience in wet chemistry techniques.

### 3.2 Health and Safety

All laboratories performing under the DNREC HSCA SOP CAP must have adequate systems and procedures to protect the health and safety of laboratory personnel.

#### 3.2.1 General Provisions

Requirement under the Occupational Safety and Health Act of 1970 (29 CFR 1910.120) and regulations promulgated pursuant thereto shall be applicable to response activities taken under these guidelines. These requirements are subject to enforcement by the designated Federal and State agencies. All governmental agencies and private employers are directly responsible for the safety and health of their own employees and compliance with those requirements. Actions taken by DNREC under these guidelines do not constitute an exercise of statutory authority within the meaning of Section (4)(b)(1) of the Occupational Safety and Health Act.

#### 3.2.2 Safety and Health Plan

Potentially responsible parties responsible for undertaking site evaluations and response activities under the 5e regulations shall submit a safety and health plan for DNREC's review and comment.

### 3.3 Basic Laboratory Equipment

Laboratory equipment must be maintained in good operating condition and be adequately calibrated prior to use on any DNREC project.

#### 3.3.1 Calibration Procedures and Frequencies

Basic laboratory equipment (e.g., balances, thermometers, meters, etc.) must be verified for accuracy against traceable, reference (e.g., NIST) standards prior to use. The verification must

be noted in a laboratory notebook or a log specific to the equipment. At least once a year, calibrations must be conducted by an external calibration service, and the servicing will be noted in the laboratory notebook or log.

#### **3.3.1.1    *Balance Calibration***

The calibration of analytical balances shall be verified on the first daily use. The quality of the weights (e.g., NIST traceable) used for calibration verification shall be documented. Balance calibration verification shall be documented in appropriate logbooks. Acceptance criteria shall be clearly identified and corrective actions taken to correct failing verifications shall be noted.

#### **3.3.1.2    *Refrigerators/freezers***

All refrigerators and freezers shall be monitored for proper temperature by measuring and recording internal temperatures on a daily basis. The calibration of all thermometers used for these measurements shall be verified at least annually against certified (e.g., NIST) thermometers. Electronic thermometers shall be calibrated at least quarterly. Temperatures shall be recorded in appropriate logbooks. Acceptance ranges shall be clearly identified and corrective actions taken to correct failing verifications shall be noted.

#### **3.3.1.3    *Pipets and Other Volumetric Glassware***

The calibration of all variable volume (e.g., Eppendorf type) pipets shall be verified on first daily use to bracket the range of use. The calibration of all fixed volume (e.g., Eppendorf type) pipets shall be verified monthly. If the calibration checks indicate that the pipet delivery volumes remain constant, then the frequency of these checks can be reduced. It is recommended that the calibration of all other volumetric glassware (flasks and pipets) be verified annually. Each calibration check shall be performed at least three times, preferably with the appropriate method solvent, and recorded in appropriate logbooks.

### **3.3.2    *Maintenance***

To avoid unnecessary delays in the processing of samples, all equipment anticipated for use on a project will be maintained in a state of readiness. Routine preventive maintenance will be performed periodically on each analytical instrument in accordance with manufacturers' recommendations. Designated laboratory personnel should be trained in routine and preventive maintenance procedures for all major instrumentation. Detailed SOPs shall be on file that describes preventive maintenance procedures and schedules. When repairs are necessary, they shall be performed by either trained staff or manufacture trained service engineers. It is generally recommended that maintenance contracts be maintained on all major analytical instrumentation, unless the laboratory has on staff an individual that has received instrumentation service training by the manufacture.

Maintenance records that document procedures performed both by internal staff and external service contractors shall be maintained for all analytical instrumentation. These records must document repair and preventive maintenance of the instruments. Each record entry must be associated with a particular instrument, either through the use of a unique identifier for each instrument, or by using a separate logbook for each instrument.

Malfunctioning equipment will be visibly tagged to prevent accidental use on DNREC projects. Following major maintenance activities, instrumental return to analytical control (e.g., meeting calibration acceptance criteria) must be demonstrated in the maintenance records prior to analysis of samples.

Backup instrumentation shall be designated in case of an extended breakdown for an analytical instrument. It is the laboratory's responsibility to have a backup plan in place to prevent the failure to meet holding times for DNREC project samples in-house. The backup plan can include the use of another DNREC approved laboratory. Prior to subcontracting any analytical work to another DNREC approved laboratory, DNREC must be informed and approval given.

### 3.4 Standard Analytical Materials

All standard solutions, including calibration standards, internal and surrogate standard solutions, spiking compound solutions, performance check mixtures, and resolution check mixtures, must be fully documented and traceable, either to neat, high purity bulk materials or to commercially available standard solutions. The preparation of standard solutions must be performed according to the procedures in the documented analytical method. The laboratory is fully responsible for analytically confirming the purity, identity, and concentration of the starting material used and for maintaining complete and accurate documentation of the preparation of all standard materials used in support of analyses performed for the DNREC.

All final working standard solutions must be verified prior to their use for sample analysis. Ideally, the verification shall be performed by comparing the responses of the standard solutions against a standard solution from an independent source. In the absence of an independent standard solution, the identity and/or concentrations of the standard solutions can be alternatively confirmed by analyzing on an instrument already calibrated with previously verified standards. The confirmation run will be successful if: (1) all intended target analytes are present and resolved (or otherwise identifiable); and (2) the concentrations calculated against the current calibration agree with the final calculated concentrations within 15%.

The analytical results for all confirmation runs shall be clearly labeled with the standard identification number, the dates prepared and checked, and a signed notation indicating whether or not the results are acceptable. The laboratory for a minimum of 2 years shall maintain this documentation; it must be readily accessible for provision to the DNREC upon request. If the working standard is not usable, a notation to this effect must be added to the standards preparation log. Documentation of the composition, purity, and/or concentration of commercially obtained materials must also be maintained by the laboratory, whether produced by the laboratory or provided by the commercial supplier. It is the responsibility of the laboratory to confirm that the materials purchased from a commercial supplier are, in fact, exactly what they are advertised to be.

Concurrent with their receipt, standard materials must be labeled with the dates of receipt and expiration. At the time of initial opening, standard materials must be labeled with the date of opening. Standards prepared in the laboratory must be labeled with the contents, initials of the preparer, date of preparation, date of expiration, and a unique identifier number to facilitate the traceability back to a standard preparation logbook. Standards must be stored consistent with manufacturer's guidelines or as required by the referenced method in order to maintain their integrity. Measurement of standard materials to prepare secondary solutions must be performed

using volumetric measuring apparatus of verified accuracy and precision over the volumetric range used. Automatic pipets (e.g., Eppendorf type), providing fixed volume and adjustable volume delivery, used to prepare standards must be checked for conformance to calibration specifications on a daily basis, prior to use. Gas tight syringes used to prepare standards must have been calibrated and demonstrated to meet acceptance criteria prior to use or been verified by the manufacturer. Final dilution volume measurement in the preparation of standard solutions must be performed in Class A volumetric glassware (e.g., volumetric flasks).

### **3.4.1 Standard Traceability**

Standard logbooks must be used to document the preparation of each standard and quality control material from original stock materials, including all subsequent dilutions. The logbook must clearly document the “recipe” followed to prepare a standard solution in such a manner to easily facilitate identification of the origin of all materials used to prepare the standard and verification of its concentration by an outside auditor. A unique identifier must be assigned to each original stock material and to each subsequent dilution used to prepare intermediate, working and daily calibration standard solutions. Logbook entries must include the prepared concentration and unique identifier of the prepared standard, the dates of preparation and expiration, the amount and the lot numbers or unique identifiers of stock materials and solvents used to prepare the standard, and the initials of the person preparing the standard.

## **3.5 Recordkeeping**

Laboratories performing under the DNREC HSCA SOP CAP must have adequate systems for maintaining and retrieving documentation associated with analyses performed on DNREC samples.

### **3.5.1 General**

The laboratory shall maintain records documenting all phases of analytical work performed; starting from the preparation and shipment of sample containers to the field, continuing with sample receipt and processing within the laboratory, and concluding with reporting of results and validation by the end user of the data. Hardcopy documents used by the laboratory shall include, but not limited to, logbooks, chain-of-custody records, sample preparation/extraction/digestion logs, bench sheets, and other documents relating to the sample or sample analysis. The laboratory shall use a document numbering and identification system for all documents/logs in order to provide an audit trail that will unequivocally enable the recreation of all activities involved in generating sample results. All records must unambiguously identify samples, standards and quality control materials used to generate the data.

All information and results recorded by the laboratory shall be made on either preprinted laboratory forms, permanently bound laboratory notebooks, or entered into secure computer systems (e.g., laboratory information management system- LIMS). Pages in both the bound and unbound logbooks shall be sequentially numbered and maintained in a manner preventing the easy removal of pages. Preprinted laboratory forms shall contain the name of the laboratory, the name of the document and the revision number. Each page of the notebook must be dated and signed by the person performing the indicated activities. Additionally, periodic review of the notebooks will take place and the reviewer, preferably the immediate supervisor, shall sign each page reviewed. All logbook entries shall be made in chronological order. All entries shall be made in indelible ink. Signature pages containing the printed name, signature and initials of all

individuals making entries into the logbook shall be included at the beginning of the document or must be available immediately upon request during an on-site audit. Any incomplete pages will be marked as such by a single diagonal line prior to dating and signing the page. Errors will be corrected by drawing a single line through the incorrect entry, dating, and initialing the change. Incorrect entries should not be obliterated. Computer forms shall contain the name of the laboratory and be dated and signed (or initialed) by the person performing the activity at the time the form is printed. Secondary reviews of computer generated forms shall be documented by the initials and date of review by the individual performing the review. Computer systems must be configured to restrict access and provide for appropriate data archiving and audit trails.

Laboratory records must be maintained in a manner that allows retrieval and review. All completed laboratory notebooks, logbooks, run logs, raw data, analytical reports, electronic tapes, data disks, and other pertinent documentation shall be stored in a secure, controlled access archive area. The laboratory shall have SOPs instructing staff on proper documentation and recordkeeping procedures, including, as discussed previously: data entry and error correction, supervisory/peer review requirements, archiving data and notebooks, and other administrative tasks.

### **3.5.2 DNREC Project files**

Project files will be established and maintained by the laboratory project manager for each DNREC project and will contain all correspondence associated with the project including records of telephone conversations and verbal agreements. All material must be dated. Of particular importance are those documents initiating the project and defining the requirements of the project. While analytical raw data (chromatograms, instrument print outs, notebooks, etc.) need not be included in the project files, references to where these materials can be located in the laboratory should be included in the project files to facilitate retrieval of the data, if necessary.

### **3.5.3 Notebooks**

Sample extraction/preparation/digestion sheets, weigh logs, and pH bench sheets will be maintained, as discussed previously, for every sample and quality control sample that requires these procedures. Copies of these documents will be included in the final data package.

### **3.5.4 Standards Preparation Log**

A standards preparation log shall be maintained and shall include the following information, as a minimum, for each solution prepared:

- Unique identification number
- Description (e.g., “stock standard-VOA gases”)
- Identification number (or source) of starting material
- Weight or volume of starting material used
- Volume and identity of dilution solvent used
- Final concentration
- Date of preparation
- Expiration date
- Storage conditions and location
- Signature of analyst preparing the solution

- Initials and date of second level reviewer

The standards preparation log must be a bound notebook with sequentially numbered pages.

### 3.5.5 Instrument Run Log

A run log must be maintained for each instrument used to analyze samples for any parameter. Instrument run logs must be maintained in such a fashion to enable a complete reconstruction of the run sequence of individual instruments to include calibration, QC checks, and sample data. The analyst performing the analyses must complete the run log in “real time”. The actual analyses performed, in chronological order, shall be recorded; the run log must contain, at a minimum, the information illustrated in Figure 7-22, Instrument Run Log. It is not necessary that this exact format be used, but it is essential that all of the indicated information be supplied. The following requirements pertain to completion of the run log:

1. All injections made during an initial calibration or 12-hour analysis period must be documented on the run log. If a particular sample is not part of the SDG or batch being reported, then the field sample number should be “censored” by overwriting “ZZZZZZZ” in that column in the copy provided in the data package; the date and time analyzed must remain legible.
2. Corrections to the log must be made by drawing a single line through the incorrect entry and inserting the correct entry nearby. Every correction must be initialed and dated by the person who records it.
3. The run log must be completed in “real time,” by the person performing the analyses on that instrument or computer generated.
4. All runs that do not meet specified criteria or that require re-analysis for any reason must be so noted on the run log, e.g. in the “Comments” column in Figure 7-22, Instrument Run Log.

Computer generated logs can be used if all preceding information is captured.

Computer/instrument printouts or other independent information can be incorporated into run logs if such printouts can be permanently affixed to the appropriate log.

### 3.5.6 Preparation Log

Preparation (digestion and extraction) logs will be established and maintained to record the processing of samples prior to instrumental analyses. The logs will list:

- Date of processing
- Samples processed
- QC samples included in the analytical batch
- Weights or volumes of the sample aliquots used
- Final volume of extract or digestate
- Standards used for spiking
- Reagents/solvents used and lot identifiers

The standard procedure for sample preparation should be addressed in a laboratory standing operating procedure (SOP) and need not be described in the preparation log. However, any deviations from the SOP must be noted in the preparation log.

### **3.5.7 Instrument Maintenance Log**

An instrument maintenance log will be required to record the maintenance performed on laboratory instruments. All maintenance operations will be recorded in the maintenance log, especially those operations requiring disassembly of the equipment or alteration of the current hardware. Service provided by an outside service engineer must be documented and relevant paperwork included in the log.

A log may be specific to a particular instrument, a group of instruments, or all instruments within the laboratory. The number of maintenance logs used by a laboratory will generally depend on the number of instruments in the laboratory and the frequency of maintenance of the instruments. The maintenance history of a given instrument, however, will be retrieved more easily if individual logs are maintained for each instrument.

### **3.5.8 Weigh Log**

A weighing log/logbook/batch sheets will be established and maintained to record the mass of the aliquots used in the analysis of solid samples and those quantities of materials used to prepare standards or solutions used in normal laboratory operations. A separate weigh log/logbook should be available for each analytical balance in the laboratory.

Weigh logs/logbook should reflect the annual (external) calibration of the balance as well as the daily (before use) calibration of the balance. The specific set of weights used for daily calibration should be identified in the log as well as the last calibration date of the set of weights.

## **4.0 SAMPLE MANAGEMENT**

The sample management process has two main components; maintaining the physical integrity of the sample and documenting that the results reported represent the conditions present at the point of sampling. The physical aspects of the sample management process include:

1. use of clean inert sampling equipment and containers to collect the sample,
2. maintaining sample preservation prior to analysis and
3. appropriately disposing of the sample and associated laboratory waste at the conclusion of the analytical work.

Standardized and consistent documentation practices for all phases of the physical process must be employed to withstand technical and legal challenges concerning data authenticity. All elements of the sample management process must be documented in SOPs.

### **4.1 Sample Containers**

#### **4.1.1 Acquisition**

As specified in the project plan, the laboratory contracted to perform chemical analyses may be required to supply sample containers for use in field sampling. The laboratory must be provided with the total number of samples, including associated QC samples, for each of the intended analyses. Generally, when a laboratory is contracted to supply sample bottles it will also provide shipping containers (coolers), blue ice packs, and chain of custody forms for use by the sampling team. The laboratory will ship these materials to the project site and include the associated cost in the overall analytical costs for the project.

Bottles and containers used for sample collection and storage can either be purchased precleaned from a commercial vendor by the laboratory or the laboratory can perform the cleaning process internally. When a laboratory provides precleaned sample containers obtained from a commercial supplier for a DNREC project, the laboratory must have procedures to maintain the supplier's lot certificates verifying the cleanliness of the sample containers and be able to correlate the individual lot certificates to the sample bottles. The certificates must specify the EPA-approved cleaning procedure used to prepare the containers and the analytical quality control performed to verify lot cleanliness.

If the laboratory performs the sample bottle cleaning internally, the procedures followed must be documented in SOPs. The SOPs must include provisions for verifying cleanliness of the containers for their intended use. The analytical verification process must incorporate the testing of container blanks that can be correlated to each batch of bottles cleaned by the laboratory. Container blanks are cleaned bottles (1% of total batch size) filled with the appropriate grade of laboratory water and the water analyzed for the analytes usually collected in that type of bottle. The analytical method used must be the one that will be used for the DNREC samples (i.e., as specified in the SAP).

If the designated laboratory does not provide sample bottles and containers, commercial suppliers of pre-cleaned containers for environmental samples can be contracted to ship the necessary materials directly to the project site. The suppliers will provide clean containers

appropriate for the intended analyses and documentation verifying them to be contaminant-free. Shipping containers, provisions for cooling the samples, and chain of custody forms will have to be supplied separately.

Appropriate sample containers may also be purchased directly from laboratory supply distributors. However, arrangements must be made for cleaning the containers prior to use. Cleaning is required to remove any traces of manufacturing materials that may interfere with the determination of contaminants of interest in the environmental sample.

Regardless of the source of the sample containers, they should be handled with caution to preclude contamination by residues on the hands or in the ambient environment. All bottles should be capped, labeled and packed in a cooler or box during shipment to the field. Bottles should be stored in an area free of the contaminants of interest under investigation at the DNREC site. Long-term storage of sampling containers in the field should be avoided, unless the stability of the storage conditions can be verified through the analysis of stored sample container blanks.

#### **4.1.2 Liquid Samples**

##### **4.1.2.1 Volatile Organic Compounds (VOC)**

The container used for collection of liquid samples for volatile organic compound analysis is a forty (40) milliliter glass vial with a septum screw cap. The septum shall have a Teflon-layered side that must be placed in the cap so that the Teflon face is toward the sample in the vial. Vials may be either clear or amber colored glass. Amber glass is preferred when photosensitive compounds are included in the list of target analytes.

When filling the vial with sample, the container should be filled completely to preclude any air space in the vial. If air spaces (or bubbles) are present in the vial, volatile compounds may escape from the sample into the air space, and analysis may yield a lower estimate of the volatile contamination in the sample.

Two forty (40) milliliter vials are routinely collected at each sampling location. One of the vials serves as a backup in case the original vial is inadvertently compromised or broken. The backup vial may also be analyzed as a field duplicate sample but, if field duplicate or other matrix QC analyses are required, a total of four (two original and two backup) sample containers should be filled.

##### **4.1.2.2 Nonvolatile Organic Compounds**

Samples for nonvolatile organic compounds are routinely collected in one liter, narrow mouth, amber glass bottles with Teflon lined lids. Amber glass is used to limit exposure of the sample to light to retard any light induced chemical reactions or decompositions. The Teflon lining is to prevent contact between the sample and the plastic cap.

While total organic carbon (TOC), total organic halogen (TOX), oil & grease, phenols and total petroleum hydrocarbons (TPH) analyses are commonly regarded as inorganic test procedures, the compounds detected in these analysis protocols are organic compounds. Consequently, the containers used for collection of samples requiring these analyses should be amber glass.

#### **4.1.2.3    *Inorganic Parameters***

Liquid samples for inorganic parameters (metals, anions, acidity, etc.) are routinely collected in 500 milliliter, narrow mouth, linear polyethylene bottles. Certain exceptions apply (e.g., elemental phosphorous) to this provision and Table 4.1 should be referred to for specific requirements on inorganic sample container use.

#### **4.1.3    *Solid Samples***

##### **4.1.3.1    *Volatile Organic Compounds (VOC)***

The sample container used for collection of solid samples for volatile organic compound analysis is a tared forty (40) milliliter glass vial with a septum screw cap, containing methanol and surrogates as defined in method 5035. The vials can contain 10 to 25 ml of methanol. If 10 ml of methanol is added, the sample size will be 5 grams. If 25 ml is added, 10 grams of soil will be the sample size. It must be noted that a 10g to 25 ml sample will meet all of the Delaware URS detection limit requirements. The septum in the screw cap has a Teflon layered side that must be placed in the cap so that the Teflon face is toward the sample in the vial.

The methanol vials must be prepared by the laboratory prior to the sampling event including the addition of surrogates. The weight of each vial will be recorded by the laboratory for future determination of analytical concentrations.

##### **4.1.3.2    *Nonvolatile Organic Compounds***

Samples for nonvolatile organic compounds are routinely collected in 500 milliliter, wide-mouth, amber glass bottles with Teflon lined lids. The amber glass is to limit exposure of the sample to light to retard any light induced chemical reactions or decompositions. The Teflon lining is to prevent contact between the sample and the plastic cap. The wide-mouth provision is to facilitate filling in the field and sub-sampling in the laboratory to permit adequate mixing for ensuring sample homogeneity prior to analysis.

While total organic carbon (TOC), total organic halogen (TOX), oil & grease, phenols and total petroleum hydrocarbons (TPH) analyses are commonly regarded as inorganic test procedures, the compounds detected in these analysis protocols are organic compounds. Consequently, amber glass containers should be used for collection of samples requiring analysis for these parameters.

##### **4.1.3.3    *Inorganic Parameters***

Solid samples for inorganic parameters (metals, anions, acidity, etc.) are routinely collected in 500 milliliter, wide-mouth, linear polyethylene bottles.

#### **4.2    *Sample Preservation and Holding Times***

It is the responsibility of the PRP (or the consultant to the PRP) to ensure that samples are properly preserved, packed and delivered to the laboratory in a timely manner. Unless the PQAP specified otherwise, sample preservation must be applied as required by the reference method. Samples to be analyzed by performance-based methods must be preserved based on the requirements of the reference method.

In general, holding time requirements come from three different sources. RCRA (SW846 protocols) and NPDES/CWA (CAWW/600 series protocols) documents state that holding times begin at the time of sample collection. The CLP SOWs state that holding times begin from Verified Time of Sample Receipt at the laboratory. ***It is the policy of DNREC that holding times begin on the day of sample collection for all methods.*** Sample preservation and holding times must be listed in the PQAP and shall be listed by analysis method and include the type and volume of sample container used and storage conditions.

The elapsed time between sample collection and when it undergoes final analysis has been demonstrated to have a significant effect on accurately determining the type and concentrations of contaminants present in the field at the time of sampling. Because holding times are a critical element in the analytical process, all DNREC project samples must meet the following holding time requirements:

- Holding times begin at the date and time of sample collection.
- Sample shipment, delivery and receipt at the laboratory must be performed in a manner that maintains sample integrity.
- Holding times are to be stated in the PQAP for each analytical method to be utilized.
- Holding times are measured in days from the date of sampling, unless the holding is based on hours.
- Extraction holding times are met when the sample is placed into the appropriate medium (e.g., extraction solvent).
- The time between completion of extraction and the beginning of cleanup and/or concentration shall not exceed 1 day (unless specified otherwise in a particular method).
- Postextraction or digestion analytical holding times begin when the sample extraction or digestion is initiated.
- Holding time ends when the analysis, resulting in reported data, has begun (i.e., semivolatile GC/MS extract is injected into the instrument). If the final reported data results from a reextraction, dilution or reinjection of the sample, this analysis must have been completed within the specified holding time.
- For organics, storage between the time of extraction, cleanup, concentration and analysis shall be above freezing to at 6°C. Storage for metals digestates can be at room temperature.

Preservatives and holding times are summarized in Table 4.1 for the indicated reference methods. Additional information concerning maintaining sample stability in specific matrix types for frequently performed analytical protocols is listed in the following sections.

#### **4.2.1 Liquid Samples**

Liquid samples are preserved according to the parameters for which they are to be analyzed. Unless noted otherwise below, samples are preserved only by cooling to 4°C. Preservatives are summarized in Table 4.1 for the indicated reference methods. Samples to be analyzed by performance-based methods must be preserved as required for the reference method unless the PQAP specifies otherwise.

#### **4.2.1.1 Volatile Organic Compounds**

Samples requiring volatile organic analyses are preserved by adding four (4) drops of concentrated hydrochloric acid to the sample in the forty (40) milliliter vial. The hydrochloric acid stabilizes volatile aromatic compounds. Preserved samples with a pH less than two (2) must be analyzed within fourteen (14) days of collection. Samples that are not preserved with hydrochloric acid or have a pH greater than or equal to two (2) must be analyzed within seven (7) days of sample collection.

#### **4.2.1.2 Metals**

With the exception of hexavalent chromium, all samples requiring metals analyses are preserved with nitric acid to a pH <2 and can be stored at ambient room temperature. Samples requiring hexavalent chromium analysis are preserved by cooling to 4°C only; no chemical preservatives are to be used. Maximum holding times for metals analyses are 24 hours for hexavalent chromium, 28 days for mercury and 6 months for all other metals.

#### **4.2.1.3 Chemical Oxygen Demand**

Samples to be analyzed for chemical oxygen demand are preserved with sulfuric acid to a pH <2 and cooled to 4°C. Maximum holding time is 28 days from sample collection.

#### **4.2.1.4 Cyanide**

Samples requiring cyanide analysis are preserved with sodium hydroxide to a pH >12 and cooled to 4°C. By maintaining the pH at this level, cyanide is maintained predominantly as the anion in solution. As the pH of the solution decreases, cyanide converts to the soluble, but volatile, hydrogen cyanide. Hydrogen cyanide (with a boiling point of 25°C) may be lost through volatilization. The maximum holding time for cyanide analysis is 14 days from sample collection.

#### **4.2.1.5 Hardness**

Samples requiring hardness analysis are preserved with nitric or sulfuric acid to a pH <2. Maximum holding time is 6 months from sample collection.

#### **4.2.1.6 Nitrogen, Kjeldahl and Organic**

Samples requiring Kjeldahl or organic nitrogen analysis are preserved with sulfuric acid to a pH <2 and cooled to 4°C. Maximum holding time is 28 days from sample collection.

#### **4.2.1.7 Nitrate/Nitrite**

Samples requiring nitrate/nitrite analysis are preserved with sulfuric acid to a pH <2 and cooled to 4°C. Maximum holding time is 28 days from sample collection. An unpreserved aliquot must be provided for samples requiring individual nitrate or nitrite analysis. The nitrite analysis must be performed on the unpreserved sample within 48 hours from sample collection.

#### **4.2.1.8 Oil and Grease and TOC**

Samples requiring oil and grease and total organic carbon analyses are preserved with sulfuric acid to a pH <2 and cooled to 4°C. Maximum holding time is 28 days from sample collection for each analysis protocol.

#### **4.2.1.9 Soil Samples**

Soil samples are preserved by cooling to 4°C. No chemical preservatives are used for any soil samples. Holding times are as documented in Table 4.1.

#### **4.2.1.10 Sample Container Labeling**

Each sample container will be labeled in the field with the following information in indelible ink:

- Project name
- Unique sample number
- Date of collection
- Time of collection
- Analysis requested
- Sampler's signature and date

When applicable, use of preprinted computer-generated sample container labels is encouraged.

### **4.3 Chain of Custody (COC)**

At the time that a sample is taken from the environment, its existence will be recorded on a chain of custody form in indelible ink. The COC will indicate the following information:

- Project name
- Unique sample numbers
- Sampling location
- Dates of collection
- Times of collection
- Number of containers filled
- Analyses requested
- Sampler's signature and date

The original COC will be placed in a waterproof pouch in the shipping container with the samples listed on the documents. Each sample in the shipping container must be accounted for on a COC, and each sample listed on the COC must be in the shipping container. The shipping container must contain signed and dated custody seals.

All COC forms accompanying DNREC samples must be signed and dated upon receipt. Copies of COCs accompanying DNREC samples must be included as part of the final data package delivered to the end user of the data, regardless of the data reporting level requested in the SAP. Any subcontracting of DNREC samples to another laboratory facility must be documented appropriately using a COC that is traceable to the original COC initiated at the time of sampling.

#### **4.3.1 Sample Shipping**

All samples under the direct oversight of DNREC will be transported from the site or the DNREC office using the HSCA approved laboratories' courier service. Commercial carriers will not be used with the following exceptions: commercial carriers may be used by the HSCA approved consultant or if samples are to be shipped from the HSCA approved laboratory to another location outside the delivery range of the laboratories' courier service. Custody seals will be required if a commercial carrier is used.

#### **4.4 Sample Receipt**

On arrival at the laboratory, the shipping container will be inspected for damage, and the integrity of the custody seals (if necessary) will be verified. Any damage or breach of security will be noted on the COC documents.

The laboratory will verify that samples are received within the required hold times. If the samples are not received within the required hold time, or if the laboratory receives the sample with insufficient time to meet hold time requirements, the laboratory must receive approval to proceed with analysis from DNREC or the DNREC approved consultant.

Using a calibrated thermometer, the laboratory will measure the temperature of each shipping container by opening the shipping container, placing the thermometer into a temperature blank located in each cooler. Care will be taken to ensure that the tip of the thermometer does not touch a sample, the wall of the cooler, or the ice. After three to five (3-5) minutes, the thermometer will be removed and read immediately. The laboratory may also use a calibrated IR gun for determining temperature. The IR gun should only be used if no temperature blank is present in the cooler. Samples received outside the 4 +/-2 °C range will require permission of the DNREC Project Manager to proceed with the analysis.

The samples will be removed from the shipping containers and organized for sample log-in. The original Analytical Services Solicitation form, sample containers, information on the sample labels, and the COC will be reviewed for consistency. The laboratory will be responsible for verifying during the sample log-in process that the samples were properly preserved in the field prior to shipment to the laboratory by measuring the pH of preserved samples (except volatile organics). The pH of volatile organics liquid samples must be checked at time of analysis and documented. Documentation of sample preservation verification should be maintained in a logbook or as part of a login checklist form that can be attached to the applicable COC documentation. If chemical preservatives are not specifically noted on the COC, the samples must be considered not preserved. All discrepancies or ambiguities will be noted on the chain of custody, and the DNREC Project Manager will be notified, both verbally and in writing, within twenty-four (24) hours.

In addition to the requirements listed above, the laboratory must include additional laboratory sample acceptance criteria in the sample receipt SOP, in order to prevent the subsequent interruption of the analytical process due to sample or project anomalies that should have been identified as part of the sample receipt process. The SOP should include or incorporate by reference (e.g., 40 CFR Part 136 sample container type, preservation, and storage conditions table), a definition of the following acceptable conditions, by type of analytical request or method, when applicable:

- minimum number of sample containers;
- appropriate size or volume sample containers;
- appropriate type of container (amber to protect sample from light) and material of construction (glass/plastic container, lid and Teflon liner, as appropriate);
- minimum amount of sample material provided (estimated by volume or mass; with requirements for QC sample aliquots addressed);
- acceptable sample conditions (e.g., no headspace observed in liquid volatile organic samples).

The laboratory will incorporate the samples into its sample log-in system (e.g., LIMS). The laboratory log-in must include the field sample identification exactly as stated on the Chain of Custody. This identification must be used to report sample data. A copy of the laboratory log-in documentation must be forwarded to the Laboratory Project Manager within twenty-four (24) hours of receipt of samples. If internal laboratory sample numbers are assigned to the samples, this information will be included. The Laboratory Project Manager will review the information for accuracy and will respond with any appropriate corrective action, if required.

#### **4.5 Internal Sample Tracking**

A record must be maintained to account for the custody of samples, extracts, and digestates within the laboratory. As samples are taken from the sample custodian for processing, the custodian must sign and date a form (e.g., Internal Chain of Custody form) indicating surrender of the sample while the processor must sign and date the same form indicating receipt of the sample. If the total sample is not exhausted in processing, the remaining portion will be returned to the sample custodian, and release and acceptance of custody will be noted by signing and dating by both parties. The custody of extracts or digestates resulting from the processing or treatment of samples must be similarly recorded. When samples, extracts, and digestates are exhausted, this factor must be recorded on the internal tracking forms to terminate the custody process for those samples. Internal COC forms may be incorporated into bound logbooks. Depending upon the sophistication of the LIMS at the facility, internal COC documentation can be completed using automated procedures (e.g., use of barcode labels and readers to record container transfers).

Except for the period of delivery by a laboratory carrier, possession of a sample must be accounted for by an unbroken chain of custody from the time of collection to the time of depletion or disposal. Inherent to this requirement is that, except for the sampler, a record of accepting custody must precede a record of relinquishing custody.

#### **4.6 Sample Storage**

All samples will be stored in secured, refrigerated (if required by the applicable analysis protocol) areas to which access is limited to the sample custodial staff. All samples and their associated extracts/digestates shall be stored under conditions that will ensure their integrity and preservation and demonstrated to be free of all potential contaminants. The temperature of refrigerated storage areas will be constantly monitored to ensure that the temperature does not vary from  $4 \pm 2^{\circ}\text{C}$  without being observed and/or recorded. This may be accomplished by recording the temperature (to  $\pm 1^{\circ}\text{C}$ ) with automatic instruments or manually checking the temperature periodically. The time period between manual checks must be less than the time

required for the temperature in the refrigerated area to rise two degrees Centigrade once the power is turned off.

Samples for volatile organic analyses will be stored in an area that is separate from samples and standards for all other parameters. Samples with known or suspected high concentrations of volatiles must be stored separately.

Standards (primary, secondary, stock solutions, and working solutions) will be stored in different refrigerators than those used for samples and extracts.

#### **4.7 Sample Disposal**

No sample, extract, or digestate will be disposed of without written permission from the DNREC or PRP Project Manager. The laboratory will provide detailed information to the appropriate Project Manager regarding the proposed disposal methods. Documentation demonstrating the appropriate disposal of all unused sample portions in accordance with all applicable local, state, and federal regulations must be available upon request by DNREC personnel.

**TABLE 4-1 SUMMARY OF BOTTLE/PRESERVATIVE/HOLDING TIME REQUIREMENTS**

<b>Parameter</b>	<b>Matrix</b>	<b>Container Specifications</b>	<b>Minimum Sample Volume</b>	<b>Preservation</b>	<b>Maximum Holding Time*</b>
Volatile Organics	Water	Amber glass , 40 mL vial with teflon faced silicon septum and open screw top	40 mL	4 drops conc. HCl, Zero Headspace, Cool 4°C	14 days (7 days if pH is >2)
	Soil	Amber glass, 500 mL wide mouth jar with teflon-faced silicon septum	100-200 g	250 mL CH <sub>3</sub> OH 625 ug each of 3 surrogates Cool 4°C	14 days
	Soil	Amber glass, 40 mL vial with teflon faced silicon septum and open screw top	40 mL	5 mL sodium bisulfite solution, magnetic stir bar, Cool 4°C	14 days
Semivolatile Organics	Water	Amber glass, 1 liter narrow mouth bottle with teflon lined cap	1000 mL	Cool 4°C	Extractions within 7 days; Analyses within 40 days of extraction
	Soil	Amber glass, 8 oz	8 oz		Extractions within 14 days; Analyses within 40 days of extraction
Pesticide/PCBs	Water	Amber glass, 1 liter narrow mouth bottle with teflon lined cap	1000 mL	Cool 4°C	Extractions within 7 days; Analyses within 40 days of extraction
	Soil	Amber glass, 8 oz	8 oz		Extractions within 14 days Analyses within 40 days of extraction
Metals	Water	Plastic 1000 mL	1000 mL	HNO <sub>3</sub> to pH<2 Cool 4°C	6 months, except Hg 28 days
Chromium VI	Water	Plastic or glass	200 mL	Cool 4°C	24 hours
Metals	Soil	Plastic or glass	8 oz	Cool 4°C	6 months, except Hg 28 days; and Cr VI 24 hours
Acidity	Water	Plastic or glass	100 mL	Cool 4°C	14 days
Alkalinity	Water	Plastic or glass	100 mL	Cool 4°C	14 days
Biochemical Oxygen Demand	Water	Plastic or glass	1000 mL	Cool 4°C	48 hours

**TABLE 4-1 SUMMARY OF BOTTLE/PRESERVATIVE/HOLDING TIME REQUIREMENTS**

Parameter	Matrix	Container Specifications	Minimum Sample Volume	Preservation	Maximum Holding Time*
Biochemical Oxygen Demand, Carbonaceous	Water	Plastic or glass	1000 mL	Cool 4°C	48 hours
Bromide	Water	Plastic or glass	100 mL	None required	28 days
Chemical Oxygen Demand	Water	Plastic or glass	50 mL	H <sub>2</sub> SO <sub>4</sub> to pH<2 Cool 4°C	28 days
Chloride	Water	Plastic or glass	50 mL	None required	28 days
Chlorine, total residual	Water	Plastic or glass	200 mL	None required	analyze immediately
Color	Water	Plastic or glass	50 mL	Cool 4°C	48 hours
Cyanide, total	Water	Plastic or glass	500 mL	Cool 4°C NaOH to pH<12 0.6g ascorbic acid	14 days
Fluoride	Water	Plastic or glass	300 mL	None required	28 days
Hardness	Water	Plastic or glass	100 mL	HNO <sub>3</sub> to pH<2 or H <sub>2</sub> SO <sub>4</sub> to pH<2	6 months
Hydrogen ion (pH)	Water	Plastic or glass	25 mL	None required	analyze immediately
Kjeldahl and organic nitrogen	Water	Plastic or glass	500 mL	Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Metals other than Chromium VI or Mercury	Water	Plastic or glass	200 mL	HNO <sub>3</sub> to pH<2	6 months
Chromium VI	Water	Plastic or glass	200 mL	Cool 4°C	24 hours
Mercury	Water	Plastic or glass	100 mL	HNO <sub>3</sub> to pH<2	28 days
Nitrate	Water	Plastic or glass	100 mL	Cool 4°C	48 hours
Nitrate-Nitrite	Water	Plastic or glass	100 mL	Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Nitrite	Water	Plastic or glass	50 mL	Cool 4°C	48 hours
Oil and Grease	Water	Glass	1000 mL	Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Organic Carbon	Water	Plastic or glass	25 mL	Cool 4°C HC1 to pH<2 or H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days

**TABLE 4-1 SUMMARY OF BOTTLE/PRESERVATIVE/HOLDING TIME REQUIREMENTS**

<b>Parameter</b>	<b>Matrix</b>	<b>Container Specifications</b>	<b>Minimum Sample Volume</b>	<b>Preservation</b>	<b>Maximum Holding Time*</b>
Orthophosphate	Water	Plastic or glass	50 mL	Filter immediately Cool 4°C	48 hours
Oxygen, Dissolved Probe	Water	Glass bottle and top	300 mL	None required	analyze immediately
Oxygen, Winkler	Water	Glass bottle and top	300 mL	Fix on site Store in dark	8 hours
Phenols	Water	Glass	500 mL	Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Phosphorus, elemental	Water	Glass		Cool 4°C	48 hours
Phosphorus, total	Water	Plastic or glass	50 mL	Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
Residue, total	Water	Plastic or glass	100 mL	Cool 4°C	7 days
Residue, filterable	Water	Plastic or glass	100 mL	Cool 4°C	48 hours
Residue, nonfilterable (TSS)	Water	Plastic or glass	100 mL	Cool 4°C	7 days
Residue, settleable	Water	Plastic or glass	1000 mL	Cool 4°C	48 hours
Residue, volatile	Water	Plastic or glass	100 mL	Cool 4°C	7 days
Silica	Water	Plastic	50 mL	Cool 4°C	28 days
Specific conductance	Water	Plastic or glass	100 mL	Cool 4°C	28 days
Sulfate	Water	Plastic or glass	50 mL	Cool 4°C	28 days
Sulfide	Water	Plastic or glass	500 mL	Cool 4°C Zinc acetate NaOH to pH>9	7 days
Sulfite	Water	Plastic or glass	50 mL	None required	analyze immediately
Surfactants	Water	Plastic or glass	250 mL	Cool 4°C	48 hours
Temperature	Water	Plastic or glass	1000 mL	None required	analyze immediately
Turbidity	Water	Plastic or glass	100 mL	Cool 4°C	48 hours

TABLE 4-1 SUMMARY OF BOTTLE/PRESERVATIVE/HOLDING TIME REQUIREMENTS

Parameter	Matrix	Container Specifications	Minimum Sample Volume	Preservation	Maximum Holding Time*
Gross alpha Gross beta Radium	Water	Plastic or glass	4000 mL	HNO <sub>3</sub> to pH<2	6 months

## **5.0 ANALYTICAL PROCEDURES**

All analytical services provided by the approved laboratory in conjunction with DNREC projects must be performed in accordance with written procedures approved by laboratory management and the laboratory QA officer. Laboratory-specific standard operating procedures (SOPs) are mandatory that fully detail the actual procedures and documentation used to implement either reference methods or internally developed performance-based methods.

### **5.1 Method Capability**

To provide analytical services on DNREC projects, a laboratory must be capable of demonstrating its ability to successfully execute the method to be used. Before analyzing DNREC samples, on a matrix-specific and method-specific basis, the laboratory must have documentation that demonstrates its ability to meet the sensitivity and precision/bias criteria in the reference method or, if applicable, other project-specific criteria. This documentation shall be maintained by the QA officer and updated at least annually as specified below.

#### **5.1.1 Initial Demonstration of Capability**

For each method performed, the laboratory will experimentally determine matrix-specific Method Detection Limits (MDLs) for each analyte as specified in 40 CFR Part 136, Appendix B. Similarly, for each method performed, the laboratory shall maintain documentation that demonstrates each analyst's ability to perform the method within the precision/bias limits as statistically-derived by the laboratory or as stated in the reference method, if applicable. Laboratory-derived acceptance criteria for performance-based methods must be at least as stringent as the reference method upon which the laboratory developed method is based. A minimum of four aliquots of a laboratory control sample shall be carried through the method at the same time. The concentration of each target analyte is measured and the results used to evaluate the method's precision and bias. Each method should be evaluated using the same matrix (spiked with all project-specific target analytes) as the samples to which the method will be applied for the DNREC project.

#### **5.1.2 Continuing Demonstration of Capability**

Each analyst shall be required to demonstrate their continuing capability to perform a method. This is accomplished by reviewing/reading the applicable SOP periodically, and whenever the method (along with its SOP) is changed significantly. The precision/bias of the method shall be demonstrated by analyzing LCS and other matrix QC check samples with each batch of samples processed.

### **5.2 Selection of Procedures**

Selection of the analytical methods to be used by the laboratory is a crucial step in ensuring that the resulting data will meet the needs of the project. Prior to initiating field activities, proper selection of the appropriate analytical methods to obtain the desired information regarding a project is imperative.

### 5.2.1 Definition of Project Requirements

The DNREC and/or PRP Project Manager must compile pertinent information about the site in order to decide which analytical protocols best suit the data quality objectives (DQOs) of a given project. DQOs shall be developed in the project planning phase and prior to the initiation of data collection. DQOs define the needed precision, accuracy, representativeness, comparability completeness and sensitivity (PARCCS) of the data. The DQOs are to be specified in the Project Quality Assurance Plan (PQAP). The objectives include not only the information provided by the analytical data collection activities but also concerns such as schedule, cost, public safety, etc.

On a project-specific basis, the PRP Project Manager (and/or DNREC, if appropriate) will provide the laboratory with analytical performance objectives derived from the project DQOs. On a target analyte and matrix-specific basis, the information provided by the PRP representative should include the following:

- MDLs (as appropriate to meet project action limit criteria, a practical quantitation limit (PQL) or reporting limit may be specified);
- Required accuracy and precision criteria at specified concentrations;
- Indication whether tentatively identified compound (TIC) reporting will be required for GC/MS analyses;
- Required turnaround times; and
- Content and format of data deliverables.

The PRP may choose to employ the services of a consultant to assist in fulfilling the PRP's responsibilities. If this is the case, the consultant must be approved by DNREC. A description of required qualifications for consultants can be found at the DNREC web site, at <http://sirb.awm.dnrec.state.de.us.consult.htm>. A link to the current list of DNREC approved consultants can also be found at that address.

The PRP Project Manager has the option of specifying analytical methods. Under the DNREC HSCA SOP CAP performance based QA program, if the methods are not specified, the laboratory may recommend the methods that are best capable of meeting project-specific requirements (i.e., DQOs) for the matrices in question.

### 5.2.2 Reference Procedures

Table 5-1, Reference Analytical Methods, contains the analytical and test methods that EPA has developed, evaluated and/or found to be acceptable for reporting data under a variety of regulatory programs. These methods are intended to promote precision, accuracy, sensitivity, specificity and comparability of analyses and test results. In the absence of project specific performance requirements, the performance criteria in reference methods apply.

### 5.2.3 Performance-based Procedures

In recognition that prescriptive methods do not always employ the best available instrument technology and/or analytical technique to meet project-specific data quality objectives (DQO) in a timely and cost-effective manner, DNREC will permit the use of performance-based methodology by laboratories conducting work under HSCA SOP CAP provisions. As such the laboratory is permitted to use either prescriptive, EPA-approved methods or performance-based

technologies provided they meet DNREC project-specific requirements, unless the PQAP specifies otherwise.

Under the performance-based method approach, the DNREC approved laboratory will have the flexibility to modify the EPA reference method (e.g., SW-846, CLP SOW, etc.) or to develop new analytical approaches, provided that the performance specifications in the reference method and project-specific requirements can be met using the modified or new method. As discussed previously, the major analytical elements affecting the applicability of performance-based protocols in DNREC projects are:

- Sensitivity
- Specificity (or target analyte selectivity)
- Accuracy (or bias)
- Precision (reproducibility)
- Quantitative performance range

Each of these elements may vary depending upon project-specific requirements. Therefore, the decision as to whether it is appropriate to employ the use of a proposed performance-based method must be based on project DQOs. The requirement of documenting the performance-based method elements falls on the laboratory seeking to employ it. The laboratory must demonstrate that the performance-based method meets or exceeds the performance specifications of the referenced method.

When well documented methods do not exist to adequately address specific matrices, interferences, specific compounds, innovative technology, project cost constraints, etc., modification of an existing method or development of a new method may be required. In these cases, the employment of a laboratory capable of performing analytical method development must be identified since not all environmental laboratories possess this ability.

### **5.3 Gas Chromatography/Mass Spectrometry (GC/MS) Methods**

The combination of gas chromatography with mass spectrometry provides an extremely powerful tool for the separation and identification of a mixture of organic compounds in a given matrix. While generally more expensive than other types of analyses, GC/MS techniques have the ability to better define the compounds present in a sample. The use of capillary column GC provides excellent separation of components while the mass spectrum yields a pattern indicative of specific compounds. Linked with a computerized data system, the mass spectrum of a compound can be rapidly matched with that of a known compound in a library of spectra. With proper calibration and internal standards, quantitative data may be obtained.

A variety of published methods are currently available for the analyses of volatile and semivolatile compounds in various matrices. Sources for these methods are:

- USEPA Contract Laboratory Program Statement of Work
- USEPA SW-846 Methods for the Analysis of Solid Waste
- USEPA Methods for the Analyses of Water and Wastewater (600 series)
- USEPA Drinking Water Methods (500 series)
- "Methanol Method" For Soils

### 5.3.1 Analytes

Unless the PQAP specifies otherwise, the compounds to be analyzed by GC/MS are as specified in Sections 5.3.1.1 and 5.3.1.2 regardless of the method selected.

#### 5.3.1.1 Volatile Organics

Volatile organics to be analyzed by GC/MS are as follows:

Dichlorodifluoromethane  
Chloromethane  
Vinyl Chloride  
Bromomethane  
Chloroethane  
Trichlorofluoromethane  
1,1-Dichloroethene  
1,1,2-Trichloro-1,2,2-trifluoroethane  
Acetone  
Carbon Disulfide  
Methyl Acetate  
Methylene Chloride  
trans-1,2-Dichloroethene  
Methyl tert-Butyl Ether  
1,1-Dichloroethane  
cis-1,2-Dichloroethene  
2-Butanone  
Chloroform  
1,1,1-Trichloroethane  
Cyclohexane  
Carbon Tetrachloride  
Benzene  
1,2-Dichloroethane  
Trichloroethene  
Methylcyclohexane  
1,2-Dichloropropane  
Bromodichloromethane  
cis-1,3-Dichloropropene  
4-Methyl-2-pentanone  
Toluene  
trans-1,3-Dichloropropene  
1,1,2-Trichloroethane  
Tetrachloroethene  
2-Hexanone  
Dibromochloromethane  
1,2-Dibromoethane  
Chlorobenzene  
Ethylbenzene  
Xylenes (total)  
Styrene  
Bromoform

Isopropylbenzene  
1,1,2,2-Tetrachloroethane  
1,3-Dichlorobenzene  
1,4-Dichlorobenzene  
1,2-Dichlorobenzene  
1,2-Dibromo-3-chloropropane  
1,2,4-Trichlorobenzene

#### 5.3.1.2 *Semivolatile Organics*

Semivolatile organics to be analyzed by GC/MS are as follows:

Benzaldehyde  
Phenol  
bis-(2-Chloroethyl) ether  
2-Chlorophenol  
2-Methylphenol  
2,2'-oxybis (1-Chloropropane)  
Acetophenone  
4-Methylphenol  
N-Nitroso-di-n-propylamine  
Hexachloroethane  
Nitrobenzene  
Isophorone  
2-Nitrophenol  
2,4-Dimethylphenol  
bis (2-Chloroethoxy) methane  
2,4-Dichlorophenol  
Naphthalene  
4-Chloroaniline  
Hexachlorobutadiene  
Caprolactam  
4-Chloro-3-methylphenol  
2-Methylnaphthalene  
Hexachlorocyclopentadiene  
2,4,6-Trichlorophenol  
2,4,5-Trichlorophenol  
1,1'-Biphenyl  
2-Chloronaphthalene  
2-Nitroaniline  
Dimethylphthalate  
2,6-Dinitrotoluene  
Acenaphthylene  
3-Nitroaniline  
Acenaphthene  
2,4-Dinitrophenol  
4-Nitrophenol  
Dibenzofuran  
2,4-Dinitrotoluene  
Diethylphthalate

Fluorene  
4-Chlorophenyl-phenylether  
4-Nitroaniline  
4,6-Dinitro-2-methylphenol  
N-Nitrosodiphenylamine  
4-Bromophenyl-phenylether  
Hexachlorobenzene  
Atrazine  
Pentachlorophenol  
Phenanthrene  
Anthracene  
Carbazole  
Di-n-butylphthalate  
Fluoranthene  
Pyrene  
Butylbenzylphthalate  
3,3'-Dichlorobenzidine  
Benzo(a)anthracene  
Chrysene  
bis(2-Ethylhexyl) phthalate  
Di-n-octylphthalate  
Benzo(b)fluoranthene  
Benzo(k)fluoranthene  
Benzo(a)pyrene  
Indeno(1,2,3-cd)pyrene  
Dibenzo(a,h)anthracene  
Benzo(g,h,i)perylene

#### **5.4 Gas Chromatography (GC) Methods**

Although GC methods provide more tenuous qualitative identification information than GC/MS methods, circumstances exist in which they may be appropriately used. The initial screening of a site to determine the presence or absence of specific contamination and the quantification of known contamination at a site can be adequately determined with GC methods. The generally lower cost of GC methods compared to GC/MS make the GC techniques more desirable if they fulfill the objectives of the analyses.

The available detectors for GC are, in general, more sensitive than GC/MS; therefore, lower detection limits are usually attainable. Additionally, some GC detectors are more sensitive and, therefore, selective towards particular compounds and may be helpful in observing compounds of interest in the presence of other potentially interfering compounds.

A variety of published methods are currently available for the analyses of volatile and semivolatile (including pesticides and polychlorinated biphenyls (PCBs)) compounds in various matrices. Sources for these methods are:

- USEPA Contract Laboratory Program Statement of Work
- USEPA SW-846 Methods for the Analysis of Solid Waste
- USEPA Methods for the Analyses of Water and Wastewater (600 series)

#### 5.4.1 Organochlorine Pesticides

Unless the PQAP specifies otherwise, the Organochlorine pesticides to be analyzed by GC are as follows: (Please Note: These compounds can be analyzed by GC/MS provided appropriate Practical Quantitation Limits are achieved.)

- alpha-BHC
- beta-BHC
- delta-BHC
- gamma-BHC (Lindane)
- Heptachlor
- Aldrin
- Heptachlor epoxide
- Endosulfan I
- Dieldrin
- 4,4'-DDE
- Endrin
- Endosulfan II
- 4,4'-DDD
- Endosulfan sulfate
- 4,4'-DDT
- Methoxychlor
- Endrin ketone
- Endrin aldehyde
- alpha-Chlordane
- gamma-Chlordane
- Toxaphene
- Aroclor-1016
- Aroclor-1221
- Aroclor-1232
- Aroclor-1242
- Aroclor-1248
- Aroclor-1254
- Aroclor-1260

#### 5.5 Inorganics

Inorganic parameters include a variety of cationic and anionic species. Analytical methods include wet chemistry determinations for specific anions to the more sophisticated ion chromatographic methods for several anions or cations. Individual metals may be analyzed with good sensitivity using flame or flameless atomic absorption (AA) spectroscopy, or many metals may be observed in a single analysis using inductively coupled plasma (ICP).

A variety of published methods are currently available for the analyses of cationic and anionic materials in various matrices. Sources for these methods are:

- USEPA Contract Laboratory Program Statement of Work
- USEPA SW-846 Methods for the Analysis of Solid Waste
- USEPA Methods for the Analyses of Water and Wastewater

## Standard Methods for the Examination of Water and Wastewater

### **5.5.1 Metals Analytes**

Unless the PQAP specifies otherwise, the following metals are to be reported:

Aluminum  
Antimony  
Arsenic  
Barium  
Beryllium  
Cadmium  
Calcium  
Chromium  
Cobalt  
Copper  
Iron  
Lead  
Magnesium  
Manganese  
Mercury  
Nickel  
Potassium  
Selenium  
Silver  
Sodium  
Thallium  
Vanadium  
Zinc

### **5.6 Other Parameters**

Acceptable reference analytical methods are published for the analyses of miscellaneous parameters that may be of interest in determining the characteristics of a site of concern. These methods include, but are not limited to, biochemical oxygen demand (BOD), chemical oxygen demand (COD), various solids determinations, acidity, alkalinity, etc. Sources for these methods are:

- USEPA Methods for the Analyses of Water and Wastewater
- Standard Methods for the Examination of Water and Wastewater

**TABLE 5-1 Reference Analytical Methods**

Analysis Parameter	Sample Matrix	Analysis Mode (1)	# of Analytes	Method (2)
Volatile Organics (VOA)	water	GC/MS	33	USEPA SOW
	soil	GC/MS	33	Methanol Method
	soil, low DL	GC/ECD,PID,Hall	33	Methanol Method
	drinking water	GC/MS	60	USEPA 524.2
Halogenated Volatile Organics	water, ww, soil	GC/HSD	39	SW-8021 (EPA 601)
Non-Halogenated Volatiles	water, ww, soil	GC/FID	6	SW-8015B
Aromatic Volatile Organics	water, ww, soil	GC/PID	8	SW-8021 (EPA 602)
Acrolein, Acrylonitrile, Acetonitrile	water, ww, soil	GC/FID	3	SW8030
Semivolatile Organics (BNA)	water,soil	GC/MS	64	USEPA SOW
Phenols	water, ww, soil	GC/FID, ECD	17	SW – 8040
Phthalate Esters	water, ww, soil	GC/FID, ECD	6	SW – 8060
Nitroaromatics & Cyclic Ketones	water, ww, soil	GC/FID, ECD	various	SW – 8090
Chlorinated Hydrocarbons	water, ww, soil	GC/ECD	various	SW – 8120
Polynuclear Aromatic Hydrocarbons	water, ww, soil	HPLC	16	SW – 8310
(PAH)	water, ww, soil	GC/FID	various	SW – 8100/Mass method
Organochlorine Pesticides/PCBs	water,soil	GC/ECD	28	USEPA SOW
	water, ww, soil	GC/ECD	26	SW – 8081
Organochlorine Pesticides only	drinking water	GC/ECD	19	Standard Methods 6630
Organophosphorous Pesticides	water, ww, soil	GC/FPD	21	SW – 8141
Chlorinated Herbicides	drinking water	GC/ECD	3	Standard Methods 6640
	water, ww, soil	GC/ECD	10	SW – 8151A
Dioxins & Furans	water, ww, soil	GC/MS	18	SW – 8280,8290
Radioactivity: Gross Alpha	drinking water	CI	1	Standard Method 7110
Gross Beta	drinking water	CI	1	Standard Method 7110
Inorganics: TAL Metals	water, soil	ICP	24	USEPA SOW
Aluminum	water, soil	ICP	1	SW- 6010B
Antimony	water, soil	ICP	1	SW- 6010B
Arsenic	water, soil	ICP	1	SW- 6010B
Barium	water, soil	ICP	1	SW- 6010B
Beryllium	water, soil	ICP	1	SW- 6010B
Boron	water, soil	ICP	1	SW- 6010B
Cadmium	water, soil	ICP	1	SW- 6010B
Calcium	water, soil	ICP	1	SW- 6010B
Chromium	water, soil	ICP	1	SW- 6010B
Chromium VI	water, soil	AA	1	USEPA 218.4

**TABLE 5-1 Reference Analytical Methods**

<b>Analysis Parameter</b>	<b>Sample Matrix</b>	<b>Analysis Mode (1)</b>	<b># of Analytes</b>	<b>Method (2)</b>
Cobalt	water, soil	ICP	1	SW- 6010B
Copper	water, soil	ICP	1	SW- 6010B
Iron	water, soil	ICP	1	SW- 6010B
Lead	water, soil	ICP	1	SW- 6010B
Magnesium	water, soil	ICP	1	SW- 6010B
Manganese	water, soil	ICP	1	SW- 6010B
Mercury	water, soil	CVAA	1	USEPA 245.1
Molybdenum	water, soil	ICP	1	SW- 6010B
Nickel	water, soil	ICP	1	SW- 6010B
Potassium	water, soil	ICP	1	SW- 6010B
Selenium	Water, soil	ICP	1	SW- 6010B
Silica	water, soil	ICP	1	SW- 6010B
Silver	water, soil	ICP	1	SW- 6010B
Sodium	water, soil	ICP	1	SW- 6010B
Thallium	water, soil	ICP	1	SW- 6010B
Tin	water, soil	ICP	1	SW- 6010B
Vanadium	water, soil	ICP	1	SW- 6010B
Zinc	water, soil	ICP	1	SW- 6010B
<b>Wet Chemistry Parameters</b>				
Acidity (as calcium carbonate)	water	E or C	1	USEPA 305.1
Alkalinity (as calcium carbonate)	water	T	1	USEPA 310.1 or 310.2
Ammonia	water	E	1	USEPA 350.2
Biochemical Oxygen Demand (BOD5)	water	T or E	1	USEPA 405.1
Carbonaceous Biological Oxygen Demand (CBOD5)	water	T or E	1	USEPA 405.1
Chemical Oxygen Demand (COD)	water	T	1	USEPA 410.1
Chloride	water	T	1	USEPA 325.3
Chlorine total residual	water	T	1	USEPA 330.3
Coliform total	water	MPN	1	Standard Method 9221
Coliform,total	water	MF	1	Standard Method 9222
Color	water	C	1	USEPA 110.2
Corrosivity	waste	G	1	SW – 1110
Cyanide	water	T	1	USEPA 335.2
Fluoride	water	E	1	USEPA 340.2
Hardness	water	T	1	USEPA 130.2
Ignitability	waste	F	1	SW – 1010
Moisture	soil	G	1	USEPA SOW
Nitrate	water	C,S	1	USEPA 352.1 or 353.3
Nitrite	water	S	1	USEPA 354.1 or 353.3
Total Kjeldahl Nitrogen (TKN)	water	T	1	USEPA 351.4 or 351.3
Oil & Grease	water	G	1	USEPA 413.1
pH	water, soil	E	1	USEPA SOW
Phenols.total	water	C	1	USEPA 420.1
Phosphate,		C		

**TABLE 5-1 Reference Analytical Methods**

Analysis Parameter	Sample Matrix	Analysis Mode (1)	# of Analytes	Method (2)
hydrolyzable	water		1	USEPA 365.2
Phosphate, organic	water	C	1	USEPA 365.2
Phosphate.ortho	water	C	1	USEPA 365.2
Phosphorus.total	water	C	1	USEPA 365.2
Reactivity & Toxicity	waste	Multiple	1	SW - 1311
Residue.total (TS)	water	G	1	USEPA 160.3
Residue.filterable (TDS)	water	G	1	USEPA 160.1
Residue.non-filterable (TSS)	water	G	1	USEPA 160.2
Residue.settleable	water	V or G	1	USEPA 160.5
Residue.volatile (VS)	water	G	1	USEPA 160.4
Silica	water, waste	C	1	USEPA 370.1
Specific conductance	water, waste	E	1	USEPA 120.1
Sulfate	water, waste	TB	1	USEPA 375.4
Sulfide	water, waste	C	1	USEPA 376.2
Sulfite	water, waste	T	1	USEPA 377.1
Surfactants (MBAS)	water, waste	C	1	USEPA 425.1
Temperature	water, waste	TH	1	USEPA 170.1
Total organic carbon (TOC)	water, waste	O	1	USEPA 415.1
Total organic halogens (TOX)	water, waste	MC	1	USEPA 450.1, SW-9020B
Total Petroleum Hydrocarbons	water, waste	S		USEPA 418.1
Turbidity	water, waste	N	1	USEPA 180.1

**1 - Analysis Mode Abbreviations**

AA = Atomic Absorption (dir aspiration)  
 C = colorimetric  
 CI = counting  
 CVAA = Cold Vapor AA  
 E = electrometric  
 F = flash point  
 G = gravimetric  
 GC/ECD = Gas Chromatography/Electron Capture Detection  
 GC/FID = Gas Chromatography/Flame Ionization Detection  
 GC/FPD = Gas Chromatography/Flame Photometric Detection  
 GC/HSD = Gas Chromatography/Halogen Specific Detection  
 GC/PPID = Gas Chromatography/Photoionization Detection  
 GCMS = Gas Chromatography/Mass Spectrometry  
 GFAA = Graphite Furnace AA  
 HPLC = High Performance Liquid Chromatography  
 ICP = Inductively Coupled Plasma  
 MC = microcoulometric  
 N = nephelometric  
 O = oxidation  
 S = spectrophotometric  
 T = titration  
 TB = turbidimetric  
 TH = thermometric  
 V = volumetric

**2 - Method References**

- USEPASOW: Contract Laboratory Program (CLP) Statement of Work, 3/90 revision
- Methanol Method: Urban, M.J., Smith, J.S., Schultz, E. K., Dickinson, R.K., "Volatile Organic Sample Preservation for a Soil, Sediment or Waste," "Waste Testing and Quality Assurance: Third Volume," ASTM STP 1075, C.E. Tatsch. Ed., American Society for Testing and Materials, Philadelphia, 1991.
- USEPA 500 Series: "Methods for the Determination of Organic Compounds in Drinking Water," Dec. 1988 and following revisions.
- Standard Methods: Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 17th Ed., 1989.
- USEPA: "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.
- SW: USEPASW-846, "Test Methods for Evaluating Solid Waste," 1986 with revisions.

## **6.0 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)**

Quality Assurance (QA) is the total integrated program for assuring the reliability of monitoring and measurement data. Quality Control (QC) is the routine application of specified procedures for obtaining prescribed performance criteria throughout the monitoring and measurement process. The overall quality assurance and quality control objectives are to implement procedures for field sampling, laboratory analysis and reporting that provide data to a degree of quality consistent with their intended use. The sample set, chemical analysis results, and interpretations must be based on data that meet or exceed the quality assurance and quality control objectives established for the DNREC project. Acceptance ranges for these objectives are generally produced by the laboratory using control charts for prescriptive reference and performance-base methods; however, depending upon unique site-driven action criteria, analytical performance limits can be set based on project-specific requirements. Variances from these target ranges normally result in the implementation of appropriate corrective measures and an assessment of the impact of these corrective measures on the usability of the data in the decision making process undertaken by the end user of the data.

Tables 5-1 and 5-2 list the reference methods recommended for sample analyses performed in support of DNREC's Hazardous Substance Clean-Up Act programs. Each of these methods has associated with it a set of quality control (QC) requirements designated to monitor laboratory performance during the analytical process and, ultimately, to allow a determination of the quality, or "usability," of the final results.

The QC specifications detailed in this section are the minimum requirements for all analyses performed for DNREC. Discussions here are not intended to take the place of the selected analytical method(s) but to clarify or supplement the methods. Where differences exist between this document and the method-specified criteria for analysis or QC, the requirements of this document shall take precedence unless waived by the DNREC project manager in writing.

### **6.1 Quality Assurance Objectives for Data Measurement**

The selection of analytical methods used by the laboratory is ultimately based on the data quality objectives (DQOs) established for the end user of the data. DQOs are an integrated set of specifications that define data quality requirements based on the intended use of the data. For the laboratory, DQO's must be translated to requirements for the PARCCS parameters (i.e., precision, accuracy, representativeness, comparability, completeness and sensitivity). Ideally, PARCCS parameters are expressed quantitatively (numerically), although at times the specifications may be qualitative. The end use of the measurement data defines the necessary PARCCS parameters, and the performance specifications for the PARCCS parameters drive the selection of the measurement methods. (e.g., lower numerical goals are set when screening protocols are desired for a project).

### **6.1.1 Precision**

Precision measures the reproducibility of measurements under a given set of conditions. Specifically, it is a quantitative measure of the variability of a group of measurements compared to their average value. Precision is usually stated in terms of relative percent difference (RPD).

The overall precision of measurement data is a mixture of sampling and analytical factors. Analytical precision is much easier to control and quantify than sampling precision. Significant historical precision performance data exists, both within an individual laboratory and in the overall analytical services industry, for the majority of individual prescriptive methods, while in contrast, sampling precision is unique to each site.

Sampling precision may be determined by collecting and analyzing collocated or field replicate samples and then creating and analyzing laboratory replicates from one or more of the field samples. The analytical results from the collocated or field replicate samples provide data on overall measurement precision; analysis results from the laboratory replicates provide data on analytical precision. Subtracting the analytical precision from the measurement precision defines the sampling precision.

### **6.1.2 Accuracy**

Accuracy measures the bias in a measurement system; it is difficult to measure for the entire data collection activity. Sources of error are the sampling process, field contamination, preservation, handling, sample matrix, sample preparation and analysis techniques. Accuracy values are typically expressed as percent recovery. Sampling accuracy may be assessed by evaluating the results of field/trip blanks, analytical accuracy may be assessed through use of known and unknown QC samples and matrix spikes.

### **6.1.3 Representative ness**

Representative ness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representative ness is a qualitative parameter that is most concerned with the proper design of the sampling program. Making certain that sampling locations are selected properly and a sufficient number of samples are collected best satisfies the representative ness criterion.

Representative ness can be assessed by the use of collocated samples. By definition, collocated samples are collected so that they are equally representative of a given point in space and time. In this way, they provide both precision and representative ness information. The representative ness criteria is best satisfied in the laboratory by making certain that all subsamples taken from a given sample are representative of the entire sample. Representative ness can be assessed in the laboratory through the analysis of sample duplicates.

### **6.1.4 Completeness**

Completeness is defined as the percentage of measurements made which are judged to be valid measurements. The completeness goal is essentially the same for all data uses; that a sufficient amount of valid data be generated. It is important that critical samples are identified in the course of a project and that plans are made to achieve valid data for them.

### **6.1.5 Comparability**

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. Sample data should be comparable with other measurement data for similar samples and sample conditions. This goal is achieved through using standard techniques to collect and analyze representative samples and reporting analytical results in appropriate units. Comparability is limited to other PARCCS parameters because only when precision and accuracy are known can data sets be compared with confidence.

### **6.1.6 Sensitivity**

Sensitivity refers to the amount of material necessary to provide a detector response that can be reliably detected or quantified. Many unique definitions exist for these limits. Specific detection limits are highly matrix dependent. To be consistent and generate/report data that is comparable, the definitions of sensitivity limits must be established in project-specific SAP and be based on DQOs for the project.

Figure 6.1 depicts the relationship between project needs, DQOs and PARCCS parameter.

## **6.2 Quality Assurance/Quality Control Plans**

### **6.2.1 Project Quality Assurance Plan (PQAP)**

A Project Quality Assurance Plan will be developed for each project of concern to DNREC. The plan will outline the strategies and procedures to be used to assist in ensuring that the technical and administrative objectives of the project are achieved in a timely, cost-effective, and technically valid manner.

The PQAP must be customized for the specific site under study and must be approved by the DNREC project manager prior to initiation of activities. The PQAP will cover the entire scope of activities for the project from initial planning to submission of final reports and will include the following sections:

- Project description
- Objectives for precision, accuracy, representativeness, comparability and completeness.
- Organization, responsibilities, and authorities.
- Sampling procedures
- Sample custody
- Calibration procedures
- Analytical methods
- Data reduction, validation & reporting
- Internal QC checks
- Audits
- Preventive maintenance
- QA reporting procedures
- Corrective actions

Any changes to the PQAP after approval by DNREC must be documented and approved by the DNREC project manager prior to use.

### 6.2.2 Laboratory Quality Assurance/Quality Control Plan

The laboratory quality assurance/quality control plan will detail the methods and procedures to be used by the laboratory to accomplish the objectives of the project. The laboratory QA/QC plan will include sections on:

- Organization, responsibilities, and authorities
- Sample custody
- Calibration procedures
- Analytical methods
- Data reduction, validation & reporting
- Internal QC checks
- Audits
- Preventive maintenance
- QA reporting
- Corrective actions

While the nature of the specific project may indicate that the routine procedures of the laboratory may suffice, the objectives and control procedures of the project must be, nevertheless, scrutinized to determine that the normal laboratory procedures are, in fact, consistent with the project strategies.

### 6.3 Quality Control Samples

Quality control samples can be used to monitor the analytical process from collection of samples through the analysis of samples. QC samples may be incorporated into the sample stream in the field, at the time the samples are logged into the laboratory tracking system, or when a batch is prepared for analysis. Laboratory internal quality control checks are designed to determine if laboratory operations are in control (i.e., operating within acceptable QC limits), and to determine the effect of the sample matrix on the data being generated.

Laboratory performance QC (i.e., internal analytical system checks) is based on the analysis of a laboratory control sample to generate precision and accuracy data that are compared to control limits. This information, along with method blank data, is used to assess ongoing laboratory performance for each method performed.

Matrix specific QC is based on the use of an actual environmental sample for precision and accuracy determinations and typically relies on the analysis of matrix spikes, matrix spike duplicates, matrix sample duplicates, serial dilutions, and surrogate standards, if applicable. This information is used to assess the effect of the matrix on the analytical data.

#### 6.3.1 Field QC Samples

Field QC samples require prior planning to determine the frequency (number) and type (blanks, spikes) to be sent from the field to the laboratory. Field QC samples are not used to monitor the variations in the laboratory but, rather, field conditions that may affect the results of the actual samples. In the laboratory, field QC samples are processed as any other field sample and, in some instances, submitted to the laboratory disguised as a real field sample.

#### **6.3.1.1 Field Blanks**

Field blanks are used to detect contamination that may occur in the process of collecting or transporting samples. A matrix similar to that being collected and known to be free of the compounds or species of concern may be used as field blank material.

Field blanks are prepared on-site by the persons who collect the samples. They will be documented on the chain of custody records as individual samples and may or may not be distinguishable as blanks. Field blanks associated with soils will also be a soil matrix, and field blanks associated with waters will be a water matrix. The relationship between a field blank and its associated samples is determined by when and/or how they were prepared in the field.

Upon receipt at the laboratory, field blanks must be treated in exactly the same manner as all of the site samples. In particular, they should be prepared, analyzed, and reported with their associated samples, i.e., in the same analytical batch.

While the intent of field blanks is to detect stray contamination in the field, they may also become contaminated in the laboratory. Observed contamination in field blanks should be scrutinized to ascertain that the contamination is, in fact, due to conditions in the field and not to contamination added at the laboratory. Comparison of the field blanks with the various laboratory blanks may assist in discriminating the source of the foreign material.

#### **6.3.1.2 Trip Blanks**

Trip blanks are routinely used to monitor for cross-contamination between samples during transport. They are normally used only for volatile organic compounds since these compounds have the greatest potential for escaping from a sample container and penetrating other sample bottle seals.

In most cases, contamination found in trip blanks should be due to another sample in the shipping container, usually of extremely high concentration, or from a less concentrated sample that has leaked. If contamination is found in a trip blank and a field sample transported with the blank is found to contain a high concentration of the same compound, results for that compound at lower concentrations in any other samples should be considered suspect due to possible cross-contamination.

#### **6.3.1.3 Field Spikes**

Although not commonly used, field spikes can monitor degradation or loss of contaminants from the field to the laboratory. Field spikes can consist of field blank spikes and/or field matrix spikes. Field blank spikes consist of placing a known quantity of a compound into a known quantity of blank matrix. Field matrix spikes consist of placing a known quantity of a compound into a known quantity of an actual field sample. Care must be taken to ensure that the spike is homogeneously distributed throughout the entire sample, especially for solid samples. The spiking for these samples is done in the field by the sampling personnel, prior to delivering the sample to the laboratory.

## 6.3.2 Laboratory QC Samples

### 6.3.2.1 Sample Batches

Samples are grouped in batches. Unless otherwise specified in the PQAP or in the method specified in the PQAP or in a method specified in the PQAP, a preparation batch is defined as those samples, including QC samples, of a similar matrix that are prepared (extracted, digested) together. This requires that all samples in a preparation batch be weighed, extracted or digested, filtered, cleaned up, distilled, heated, etc., concurrently. The only times that samples in a given analytical batch can be processed sequentially is when the samples are processed through an instrument, e.g., gel permeation chromatography.

Unless otherwise specified in the PQAP or in the method specified in the PQAP or in a method specified in the PQAP, an analysis batch is defined as those samples that are processed together through the entire analytical method. The only times that samples in a given analytical batch can be processed sequentially is when the samples are processed through the measuring instrument. The processing of samples through sequential instruments must not be interrupted by alterations to the instrument such as re-calibration or maintenance.

For each analysis fraction, the QC samples for a batch must be processed with the associated samples as a set throughout the analytical procedure. Processing samples (i.e., field samples, lab blanks, lab spikes) by the defined batches not only ensures the best direct comparison between sample and associated QC results but also greatly simplifies data review, compilation, and generation of the final data package and, ultimately, streamlines the data package itself.

### 6.3.2.2 Blanks

The purpose of blank analyses is to identify possible sources of contamination that may affect the associated samples, causing elevated or false positive analyte levels to be reported when, in fact, the analyte is not a true sample component. Several typical target compounds (methylene chloride, chloroform, benzene, bis(2-ethylhexyl)phthalate, and 2-butanone, for example) are also common laboratory contaminants; only by analyzing sufficient and appropriate blanks can valid conclusions be drawn about whether these compounds are true sample components or simply procedural artifacts. To be properly associated with an analysis batch, blanks must be: (1) collected/shipped at the same time (field blanks); (2) prepared at the same time (method blanks); or (3) analyzed on the same shift (volatile method blanks for waters or instrument blanks).

#### 6.3.2.2.1 Blank Matrices

Ideally, all blanks (both field and laboratory initiated blanks) associated with the samples from a particular site will be prepared from the same source of contaminant-free (“pure”) water or soil. The origin (source and/or preparation) of all blank matrices shall be fully documented in the data package as described in Section 7.0.

##### 6.3.2.2.1.1 Water

Whenever possible, a source of water (ground or surface, as appropriate, depending on the nature of the site samples) local to the site shall be identified for use in the preparation of all blanks (field and laboratory) associated with water samples from the site. Prior to its use, the water from the identified source will be demonstrated (by analysis) to be contaminant-free, i.e. free of all target compounds for the parameters to be analyzed and free from matrix interferences.

Results of the confirmation analyses shall be documented in the data package, as described in Section 7.0. If the volume of blank water obtained prior to the confirmation analysis is not sufficient to complete the site work, then an additional confirmation analysis must be performed each time another volume of blank water is collected.

If a source of local, contaminant-free water cannot be identified or is not available, then laboratory-prepared distilled/deionized water shall be used for all blanks. This water shall, on a regular basis, be demonstrated to be contaminant-free by analysis of all applicable parameters. Results of the confirmation analyses shall be documented in the data package, as described in Section 7.0.

#### **6.3.2.2.1.2 Soil**

Unless otherwise specified in the PQAP or in the method specified in the PQAP or in a method specified in the PQAP, it is mandatory that a solid matrix be used for all blanks associated with solid samples. A source of local soil, similar in particle size distribution and general geologic characteristics to the site samples, must be identified and analyzed to demonstrate that it is free of all target compounds in the applicable analysis fractions and that it is free from matrix effects. Results of these confirmation analyses must be documented in the data package as described in Section 7.0.

If no contaminant-free local soil is available, then a volume of purchased soil/sand with particle size and geologic characteristics similar to the site samples must be ashed (in an autoclave or muffle furnace, overnight minimum) to remove the organic materials. The ashed soil must then be analyzed to confirm that it is both contaminant-free and interference-free prior to its use for blank preparation. Results of the confirmation analyses shall be documented in the data package as described in Section 7.0. Metals analysis should continue to use reagent water blanks because metals free soil is virtually impossible.

#### **6.3.2.2.2 Method Blanks**

A method blank (MB) is a volume of “pure” water when prepared in association with water samples; a method blank associated with solid samples is prepared using a “pure” solid matrix. The volume or weight used to prepare the method blank for either matrix must be approximately equal to the volume or weight used for the samples in the associated analysis batch. The method blank in each batch must be carried through the same procedures as the samples, at the same time as the samples, including (as appropriate) aliquot measurement, extraction, concentration, clean-up, and analysis.

##### **6.3.2.2.2.1 Frequency Requirements**

Unless otherwise specified in the PQAP or in the method specified in the PQAP or in a method specified in the PQAP, a minimum of one (1) method blank shall be prepared with every extraction batch (volatiles in soil, semivolatiles, pesticide/ PCB's, inorganic) of up to 20 samples, regardless of how few samples are in the batch. A minimum of one (1) method blank shall be prepared and run on every 12-hour shift and instrument where waters are analyzed for volatiles.

The method blank for a batch must be analyzed with its associated samples, ideally under the same calibration standards. Unless otherwise specified in the PQAP or in the method specified

in the PQAP or in a method specified in the PQAP, the following rules apply to the order and frequency of method blank analyses for all analysis fractions:

- For volatiles analysis, a method blank will be run on every instrument on every 12-hour shift on which samples are run. The volatiles method blank shall be run after the successful BFB tune and continuing calibration standard and before any samples are analyzed.
- For all analyses of sample extracts (volatiles in soil, semivolatiles, pesticides/PCB's, inorganics), the method blank extracted with the batch shall be run on every instrument used to analyze the samples, on every 12-hour shift where samples are run. Note that the method blank from an extraction batch must be run as many times as necessary to satisfy this requirement.

#### 6.3.2.2.2.2 *Acceptability Criteria*

No contaminants of any kind should be present in the laboratory method blanks. However, there are several compounds known to be common lab contaminants that are difficult to keep out of the blanks. These are methylene chloride, acetone, toluene, and 2-butanone for the volatile fraction, and phthalate esters for the semivolatile fraction. Unless otherwise specified in the PQAP or in the method specified in the PQAP, a method blank will be considered acceptable when the following conditions are met:

- For volatile analysis, the method blank must contain less than or equal to five times (5x) the method-specified detection limit of methylene chloride, acetone, toluene, and 2-butanone. All other target compounds must be less than or equal to the method-specified detection limit.
- For semivolatile analysis, the method blank must contain less than or equal to five times (5x) the method-specified detection limit of each phthalate ester (bis(2-ethylhexyl) phthalate is most commonly found); all other target compounds must be less than or equal to the method-specified detection limit.
- For pesticide/PCB analysis, the method blank must contain no single target analyte.
- For all analyses performed by GC/MS, the method blank should contain no extraneous peaks greater than 10% of the peak height of the nearest internal standard peak. This excludes aldol condensation products and solvent artifacts in the semivolatile fraction.
- For inorganics analyses other than metals, no contamination should be observed in the method blanks greater than the method detection limit. For metals, no contamination should be observed above the laboratory practical quantitation limits.

If a method blank does not meet these criteria, then corrective action, dependent on the effect of contamination, must be taken and documented. All samples processed with a contaminated method blank may have to be re-extracted (or re-digested) and re-analyzed if the project requires determinations of parameters at concentrations that are near or below the level of contamination observed in the method blanks.

When reporting results for samples associated with a contaminated method blank, sample results will not be corrected for the blank contamination. Instead, the affected data will be flagged as having been analyzed with a method blank having significant contamination relative to the sample result.

#### 6.3.2.2.2.3 *Documentation*

Results of method blank analyses shall be reported on Organics Analysis Data Sheets (Figures 7-7 and 7-8). In addition, the Method Blank Summary Form (Figure 7-4) shall be completed to identify samples associated with each method blank.

#### 6.3.2.2.2.4 *Nomenclature*

The following method blank naming conventions shall apply:

- Within a batch, all method blanks must be uniquely identified; VBLK1, VBLK2, VBLK3, SBLK1, SBLK2, SBLK3, and PBLK1, PBLK2, PBLK3 would be used to identify 3 separate method blanks prepared and run for volatiles, semivolatiles, and pesticide/PCB's, respectively, in a single batch for each fraction.
- When a method blank is run more than once, i.e., to meet the criterion set forth in Section 6.4.2.2.2.1 above, it should be noted in the case narrative or instrument logbook..

The designations specified above shall be used as the “field” or “client” sample numbers for method blanks when completing all summary forms to be included in the data package.

#### 6.3.2.2.3 *Storage Blanks*

Storage blanks are a special kind of laboratory blank that are used specifically to evaluate the conditions under which samples for volatiles analysis are stored for cross-contamination potential.

A storage blank consists of 40 mL of laboratory-prepared distilled/deionized water in a VOA sample vial. The vial is carefully sealed, and held in the VOA storage refrigerator for a minimum of 24 hours prior to its analysis. Unless otherwise specified in the PQAP or in the method specified in the PQAP, a storage blank from each separate VOA storage area must be analyzed at least once a week. The analytical results for the storage blank(s) associated with the samples in a given project must be included in the deliverables package, as described in Section 7.0.

#### 6.3.2.3 *Spikes*

Recovery of selected target compounds from spiked (“fortified”) blanks or samples in each analysis fraction is monitored to evaluate the overall performance of the analytical method.

##### 6.3.2.3.1 *Matrix Spike*

A matrix spike (MS) is a second aliquot of an actual field sample that is fortified with the spiking compounds during preparation for analysis. A matrix spike sample is prepared at the same time as the original, unspiked sample, and allows evaluation of possible matrix effects that may interfere with the analytical method.

##### 6.3.2.3.1.1 *Frequency Requirements*

Unless otherwise specified in the PQAP or in a method specified in the PQAP, a matrix spike is prepared and analyzed at a minimum frequency of one (1) with every preparation or analysis batch (as appropriate) of up to 20 samples of a similar matrix. The sample to be used for the MS analysis will be so indicated on the chain of custody records received with each set of samples.

If no sample is indicated for MS analysis on the chain of custody, then the laboratory must immediately call the Project Manager to confirm that no project-specific MS is required with that set of samples.

Even if not requested on a project-specific sample, a MS sample must still be prepared and analyzed with every preparation or analysis batch of up to 20 samples of a similar matrix. When the sample used for this purpose is not project-specific, the results shall be reported without identification of the source of the sample used.

#### *6.3.2.3.1.2 Specifications and Recovery Limits*

Unless otherwise specified in the PQAP or in a method specified in the PQAP, Table 6-1, Matrix Spike Recovery Limits, lists the compounds that shall be used to prepare matrix spiking solutions and the recovery limits against which the results will be evaluated. Unless otherwise specified in the PQAP or in the method specified in the PQAP or in a method specified in the PQAP, spiking levels shall be approximately 5-10 times the specified method detection limit for each spike compound. In lieu of the specified QC limits, the laboratory may utilize statistical derived laboratory limits, provided they are updated once a year.

#### *6.3.2.3.2 Matrix Spike Duplicates*

A matrix spike duplicate (MSD) sample is prepared in exactly the same manner as the MS sample, using the same original sample, at the time the analytical batch is prepared. Unless otherwise specified in the PQAP or in a method specified in the PQAP an MS/MSD pair is included with every analytical batch of up to 20 samples of a similar matrix for all organic parameters (volatiles, semivolatiles, pesticides/PCB's). The use of an MS/MSD pair ensures that there will always be positive duplicate results for comparison. Therefore, a reasonable estimate of the method precision (as measured by the RPD) can be obtained.

Unless otherwise specified in the PQAP or in a method specified in the PQAP, MSDs are used only for organic analyses. Also unless otherwise specified in the PQAP or in a method specified in the PQAP, frequency, specifications, and recovery criteria for the MSD are the same as described in Table 6.1 for the MS. Unless otherwise specified in the PQAP or in the specified method in the PQAP upper limits for relative percent difference (RPD) values comparing each paired set of spike compound results are given in Table 6.2.

#### *6.3.2.3.2.1 Actions Required Based on Paired MS/MSD Results*

Since MS/MSD recovery results are intended primarily for evaluation of possible matrix effects, unless otherwise specified in the PQAP or the method specified in the PQAP, no reanalysis requirements are specified based on the recovery results for the spiked compounds alone. However, the following situations may indicate a procedural or system problem, rather than a matrix effect:

- Most or all recoveries for either the MS or the MSD are outside the limits while the concentrations of other components in the paired samples are within limits.
- Recoveries for one or more spike compounds are outside the limits in both the MS and MSD runs of a pair but the RPD is within the specified limit.

When either of these situations or a similar occurrence is observed, the laboratory is required to identify the likely causes (e.g., poor spiking technique or degradation of the spiking solution) and

take appropriate corrective action to prevent its recurrence. A discussion of the surmised causes and the corrective actions taken shall be included when reporting the results.

#### 6.3.2.3.2.2 *Documentation of the MS/MSD Results*

Results of MS/MSD analyses shall be reported on an Organic Analyses Data Sheet (CLP Form 1 or equivalent). In addition, the MS/MSD Recovery Summary (CLP Form 3 or equivalent) shall be completed for each pair.

#### 6.3.2.3.3 Blank (Method) Spikes

A spiked blank sample will allow evaluation of the overall effectiveness of the analytical method as performed on a given day but can provide no information regarding possible matrix effects in the associated samples. Unless otherwise specified in the PQAP or in the method specified in the PQAP, a blank spike must be analyzed with every analytical batch and analytical sequence as the MS/MSD.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, a blank spike/blank spike duplicate (BS/BSD) pair must be analyzed with each analytical batch if sample is unavailable to analyze a MS/MSD. A BS/BSD pair must be of the same matrix (soil or water) as the samples in the batch. Recoveries of the BS/BSD compounds must meet the QC requirements given in Tables 6-1 and 6-2.

#### 6.3.2.4 *Duplicates*

A duplicate sample is a second aliquot of a field sample that is measured and processed with the analysis batch in exactly the same manner as the rest of the field samples. Unless otherwise specified in the PQAP or in the method specified in the PQAP, any parameter not listed in Table 6-1 is analyzed in duplicate. For all inorganics parameters, a sample (matrix) spike and a sample duplicate (instead of an MS/MSD pair) are prepared at the same time the analytical batch is prepared.

##### 6.3.2.4.1 Frequency Requirements

Unless otherwise specified in the PQAP or in a method specified in the PQAP, a duplicate sample is prepared and analyzed at a minimum frequency of one (1) with every preparation or analysis batch (as appropriate) of up to 20 samples of a similar matrix. The sample to be used for the duplicate analysis may be so indicated on the chain of custody records received with each set of samples. If no sample is indicated for duplicate analysis on the chain of custody, then the laboratory must immediately call the Project Manager to confirm that no project-specific duplicate is required with that set of samples.

Even if not requested on a project-specific sample, a duplicate sample must still be prepared and analyzed with every preparation or analysis batch of up to 20 samples of a similar matrix. When the sample used for this purpose is not project-specific, the results shall be reported without identification of the source of the sample used.

#### 6.3.2.4.2 Precision Specifications for Duplicate Samples

Unless otherwise specified in the PQAP or in a method specified in the PQAP, Table 6-3, Duplicate Sample Precision Limits, lists the RPD limits against which the results will be evaluated.

#### 6.3.2.4.3 Actions Required Based on Duplicate Sample Results

Unless otherwise specified in the PQAP or in the method specified in the PQAP, no reanalysis requirements are specified based on the results for duplicate samples alone.

#### 6.3.2.4.4 Documentation of Duplicate Results

Results of duplicate analyses shall be reported on CLP Form 6 or equivalent.

### 6.4 Sample Preparation

#### 6.4.1 Volatiles in Water

Preparation of water samples for analysis of volatiles by GC or GC/MS requires accurate measurement of the sample aliquot (volume) to be purged, as specified by the selected analytical method. Sample volumes actually purged must be recorded by the analyst in the Instrument Run Log in “real time,” i.e., when the sample is analyzed. Sample volumes should not be recorded in advance of sample analysis (assuming that the usual volume will always be used) or long after analysis (when memory must be relied upon).

#### 6.4.2 Volatiles in Soil

When using the methanol method, all soil/sediment samples for volatiles analysis must be prepared and analyzed according to the method in Appendix B. Sample containers must be prepared and weighed (at the same laboratory that will perform the subsequent analysis) as described in the method prior to being transported to the field. The following QC requirements will apply:

- The balance used to weigh the sample bottles must be calibrated as described in Section 7 of this document.
- The same balance must be used for both the “before” and “after” weight measurements of each bottle. It is also highly preferable that the same analyst perform both the before and after measurements for each bottle.
- Each sample bottle must be labeled with a unique identifier before it is transported to the field. This identifier may be used as the laboratory sample ID upon the sample’s return for analysis, or it may be a different descriptor, at the discretion of the laboratory.
- “Before” and “after” sample bottle weights shall be recorded by the analyst who performs the measurements in the Sample Extraction Log (Figure 3-1), which will contain, at a minimum, the illustrated information. It is not necessary that this exact format be used, but it is essential that all of the indicated information be provided.
- Separate sample bottles for MS/MSD samples must be prepared concurrently with all of the bottles prepared for a sampling event, and must be similarly documented. The required frequency is a minimum of one (1) MS/MSD pair for every 20 samples.

- The bottles containing sample aliquots from the same location will be labeled “for MS” and “for MSD” on the chain of custody record; the third sample from that location, to be unspiked, shall be labeled “MS/MSD Original” on the chain of custody. The indicated samples must be used to perform the MS and MSD analyses.
- The Methanol field preservation method is mandatory for non-aqueous samples.

### **6.4.3 Semivolatiles and Pesticide/PCB's**

Preparation of samples for semivolatiles or pesticide/PCB analysis requires extraction of the sample with an organic solvent. Procedures must be carefully controlled to minimize laboratory contamination and ensure consistency of performance. Documentation of all steps is crucial to ensuring calculation of an accurate final result as well as to allowing investigation of possible sources of error or interferences when problems are encountered. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following QC requirements will apply to all sample extractions:

- All extractions shall be documented on a Sample Extraction Log.
- A Method Blank (MB) shall be prepared with every extraction batch.
- One (1) matrix spike/matrix spike duplicate (MS/MSD) pair shall be prepared with every extraction batch.

### **6.4.4 Surrogate Standards**

For all organic parameters, surrogate compounds are added at known concentrations to all samples and blanks prior to preparation (purging or extraction). In the case of volatiles in soil, the surrogates are added to the methanol in the sample container prior to measurement of the “before” weight. Measurement of surrogate recoveries is used to monitor laboratory and method performance on each individual analysis.

Surrogate compounds for volatiles analysis are referred to as “System Monitoring Compounds” in the CLP SOW; this is primarily a semantic distinction and does not affect the choice of surrogate compounds or the procedures used.

#### **6.4.4.1 Specifications**

Unless otherwise specified in the PQAP or in the method specified in the PQAP, the surrogate spiking compounds (at the indicated levels) listed in Table 6-4 shall be used to fortify each sample, blank, matrix spike, and matrix spike duplicate prior to its preparation and analysis.

#### **6.4.4.2 Acceptability Criteria**

All surrogate compound results must be checked as each analysis is performed. Measured concentrations must be converted to percent recovery. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the recoveries are to be evaluated against the recovery limits listed in Table 6-5, Acceptance Limits for Surrogate Recoveries or laboratory generated acceptance limits.

#### **6.4.4.3 Actions Required Based on Surrogate Recoveries**

If the surrogate recoveries for all samples and MB's for the applicable fractions in a batch are within the acceptability criteria specified in the Table 6-5 (Unless otherwise specified in the PQAP or in the method specified in the PQAP), no corrective action is required.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, if any surrogate recoveries in a method blank or sample are outside the applicable acceptance limits, the following actions must be taken in the order specified:

- No surrogate recoveries are permitted outside Quality Control Limits in a Method Blank, Aqueous Field Blank, Trip Blank, and Equipment Blank unless gross contamination is carried over from field operations. Re-extraction and re-analysis must occur, if acceptable quality control limits are not met. Field Blanks requiring the methanol method do not require re-extractions.
- Check calculated recoveries for errors; re-evaluate corrected recoveries against acceptable limits if errors are found.
- Re-analyze all of the extracts including blanks, spikes, etc., on a successfully tuned and calibrated instrument. If surrogate recoveries are satisfactory, report these results.
- Check the integrity of the surrogate and internal standard spiking solutions used by making individual injections on a successfully tuned and calibrated instrument. Results of these injections must be available at DNREC's request.
- If significant degradation or contamination of either solution is confirmed, then all samples in the affected batches must be re-extracted (where applicable) and re-analyzed using new solutions. There are no advisory surrogate limits. Note: Re-extraction is not possible for volatiles in soil.
- If only a slight concentration variation in the surrogate standard solution (i.e., the solution is more or less concentrated than usual, for one or more compounds) is determined to be the cause of the surrogate recoveries being outside the QC limits, then re-extraction and/or re-analysis are not required. In this case, a complete explanation of the situation and the supporting analytical data must be provided when reporting the data.
- If the integrity of both solutions is confirmed, then all affected samples must be re-extracted (where applicable) and re-analyzed. Note: Re-extraction is not possible for volatiles in soil.
- If surrogate recoveries are still outside acceptance limits, report both sets of data clearly labeling which is the original and which is the rerun.
- The laboratory is permitted one surrogate outside of quality control limits per semivolatile fraction provided their recoveries are greater than ten percent.

#### **6.4.4.4 Additional Surrogate Requirements for Methods Blanks**

Method blanks must generate surrogate recoveries within the specified acceptance limits. Since no matrix effects are possible if the method blank matrix is distilled water, any deviations must be considered to be due to problems within the laboratory's control.

For volatiles, sample analyses shall not proceed on any 12-hour shift until a method blank with acceptable surrogate recoveries is analyzed following the successful tune and calibration. For semivolatiles and pesticide/PCB's, all samples associated with the affected method blank must be re-extracted and re-analyzed after successful corrective action has been taken and documented.

#### **6.4.4.5 Documentation**

Surrogate recovery data must be reported as Percent Recovery for all original and rerun analyses of all MB's, samples, and MS/MSD sample pairs on the Surrogate Spike Recovery Summary (CLP Form 2 or equivalent).

#### **6.4.5 Inorganics**

Preparation of samples for inorganic parameters varies considerably depending on the analysis. Specified procedures must be followed carefully to ensure that the method performs as designed. If the procedures used deviate from the specified method, the deviations must be well documented and reported with the analytical results.

Vigilance must be constantly practiced during the preparation of samples to ensure that the methods are appropriately applied. For example, in the digestion of metals for analysis by AA or ICP, a stated quantity of acid is used to oxidize the metals. If the sample contains organic material, they may be preferentially oxidized at the expense of the metals. Consequently, a determination of the metals may yield a value considerably lower than the actual concentration. Sufficient acid must be added during digestion to oxidize any organic matter, as well as all metals, completely. If an oily film is present in a digested sample, this may be evidence that excess organic material is present in a sample. If the sample emits smoke from the carbon tube during analysis in a furnace AA, excess organic material can also be assumed to be present.

In many cases, careful inspection of the sample prior to digestion may reveal a situation requiring a modification of the written method. If an optical measurement is being made (e.g., spectrophotometric methods), care should be taken to ensure that the optical beam has a clear path through the sample. The analyses of samples for inorganic parameters require not only the ability to read and perform a documented method but also the understanding of the principles involved in the method.

### **6.5 Calibration**

#### **6.5.1 GC/MS Calibration**

Calibration allows generation of quantitative results according to specific procedures on a particular instrument; QC criteria defining satisfactory initial calibration are designed and monitored to ensure that the instrument is capable of producing acceptable (i.e., consistent and accurate) results for that method under the current conditions. QC criteria defining satisfactory continuing and ending calibrations are designed and monitored to ensure that instrument responses remain consistent enough to allow accurate qualitative and quantitative evaluation of sample results during the current analysis shift.

##### **6.5.1.1 GC/MS Instrument Performance**

Prior to the analysis of any standards, blanks, or samples, the GC/MS must be tuned to ensure satisfactory instrument performance; specifically, to ensure appropriate mass resolution, mass identification, and sensitivity. The mass spectrum of a method-specific tuning compound is also evaluated on a regular basis to verify continuing acceptable instrument performance.

###### **6.5.1.1.1 Tuning Specifications**

For volatiles analysis, the tuning compound is bromofluorobenzene (BFB); for semivolatiles, decafluorotriphenylphosphine (DFTPP) is used. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements apply for both analysis fractions.

- The tuning compound shall be injected at the start of every 12-hour analysis period.
- If any maintenance or repairs are performed on the instrument, BFB/DFTPP shall be injected prior to re-initiating sample or standard analyses regardless of the length of time since the last tuning run.
- Analysis of standards or samples shall not continue until and unless acceptable results are obtained for the tuning compound analysis.

#### 6.5.1.1.2 Acceptability Criteria

Unless otherwise specified in the PQAP or in the method specified in the PQAP, the BFB or DFTPP mass spectrum for evaluation must be generated as follows:

- Average together three scans: the scan at the BFB/DFTPP peak apex, the scan just before the apex, and the scan just after the apex.
- Subtract a single scan from before the elution of the BFB/DFTPP peak to remove background contributions.

Calibration and sample analysis may not continue until the relative abundance criteria for the tuning compound have been met in a correctly-generated spectrum.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, acceptable instrument performance has been demonstrated only when the correctly generated mass spectrum for the tuning compound meets the relative abundance criteria set forth in Table 6-6 for BFB and 6-7 for DFTPP.

#### 6.5.1.1.3 Documentation

BFB/DFTPP tuning results shall be summarized on a GC/MS Instrument Performance Check form (CLP Form 5 or equivalent).

The reconstructed ion chromatogram (RIC), mass spectrum, and mass listing must be provided in the data package, as described in Section 7.0.

### 6.5.1.2 Initial Calibration

QC criteria defining satisfactory initial calibration are designed and monitored to ensure that the instrument is capable of producing acceptable (i.e., consistent and accurate) results for that method. Initial calibration establishes that an instrument is capable of acceptable performance at the start of the analyses.

#### 6.5.1.2.1 Initial Calibration Specifications

Initial calibration (IC), or demonstration of linearity of response, shall be performed for all GC/MS methods as prescribed in the selected analytical method with respect to required standard concentrations and the specific analytes to be calibrated. Unless otherwise specified in the

PQAP or in the method specified in the PQAP, the following requirements shall apply to initial calibrations for all GC/MS analyses performed in support of projects for the DNREC:

- An IC shall be performed on every instrument used to analyze samples.
- An IC must be established (or re-established) on each instrument:
  - Prior to any sample analyses;
  - Whenever a new column is installed;
  - Whenever instrument adjustments that affect sensitivity are made;
  - Whenever a continuing calibration standard does not meet the specified acceptance criteria; and
  - Whenever the selected method has not been performed on that instrument for more than 30 calendar days.
- The IC on each instrument must immediately follow an acceptable tuning compound analysis.
- The IC must consist of a minimum of five (5) standard concentration levels.
- The Relative Response Factor (RRF) for each individual analyte at each concentration shall be calculated as required in the current version of the CLP SOW; characteristic ions used for RRF calculations shall be as prescribed in the CLP SOW.
- For target analytes not specified in the CLP SOW, a quantitation ion must be selected that is free of interferences from closely eluting peaks and that is either the molecular ion or has a relative abundance of at least 50% of the molecular ion.
- If an area is incorrectly integrated by the data system, then a manual integration shall be performed and documented by the analyst: a hard copy of the manually integrated quantitation ion peak (showing the integration lines and the resulting area) must be included in the data package, the manual area must be recorded on the quantitation report, and an “M” must be appended to the quantitation report entry.
- The RRF for each standard level, the average RRF, and the % RSD shall be documented on the GC/MS Initial Calibration Data form (Figure 7-9), or a similar form. All of the indicated information must be provided on the form used.

#### 6.5.1.2.2 Initial Calibration Acceptability Criteria

Unless otherwise specified in the PQAP or in the method specified in the PQAP, an acceptable IC will meet the following criteria:

- All analytes are detected at all levels, except where specifically stated otherwise in the selected method.
- The average RRF is  $\geq 0.10$  for all volatile analytes.
- The average RRF is  $\geq 0.05$  for all semivolatile analytes.
- The % RSD for each analyte is  $\leq 30\%$ .

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***Note: Unless otherwise specified in the PQAP or in the method specified in the PQAP, the use of linear regression or other calibration curves in lieu of use of mean RRFs is NOT acceptable to DNREC.***

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If the above criteria are not met following analysis of the series of IC standards, then the following actions shall be taken:

- If a bad injection or instrument malfunction is suspected, then the affected standard(s) shall be re-analyzed; acceptable standard runs for all IC levels and the IB must be generated within a maximum time period of 12 hours, starting with the injection of the tuning compound.
- The working calibration standard solutions should be checked (by separate injection on a different instrument) to determine if degradation, concentration, or contamination has occurred.
- Appropriate corrective action, as determined by the laboratory, shall be taken and documented.
- The IC sequence must be repeated until acceptable results are obtained.

An acceptable IC is mandatory before sample analysis may proceed.

#### **6.5.1.3 Continuing Calibration**

Once the IC is successfully established on an instrument, sample analyses may begin. Continuing calibration standard checks are performed at regular intervals to ensure that instrument responses remain sufficiently consistent to allow accurate qualitative and quantitative evaluation of sample results.

##### **6.5.1.3.1 Continuing Calibration Specifications**

Continuing calibration (CC) standards at or near the mid-point of the IC range shall be prepared and analyzed for all GC/MS methods as prescribed in the selected analytical method. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements shall apply to CC's for all GC/MS methods performed in support of projects for the State of Delaware.

- A CC shall be performed, at a minimum, at the start of every 12-hour shift on every instrument on which samples are analyzed.
- The CC shall include, at a minimum, the following analyses in the specified order:
  1. Tuning compound;
  2. Calibration standard; and
  3. Method blank.
- The calibration standard shall be at or near the mid-point of the IC range.
- The 12-hour shift begins when the successful tuning compound run is injected. Standards, samples, and blanks may be analyzed under this tune until 12 hours have elapsed on the system clock.
- The RRF for each individual analyte must be calculated exactly as it was calculated in the associated IC; requirements for quantitation ions and for documentation of manually integrated areas are the same as described in Section 6.5.1.2.1.

##### **6.5.1.3.2 Continuing Calibration Acceptability Criteria**

Unless otherwise specified in the PQAP or in the method specified in the PQAP, an acceptable CC for all GC/MS analyses will meet the following criteria:

- The tuning compound analysis must generate acceptable results, as described above.

- All target analyte RRF's must be  $\geq 0.10$  for volatile organic compounds and  $\geq 0.05$  for semivolatile organic compounds, for both the initial and shift-ending calibration standards. Any variances from these requirements must be approved by the DNREC.
- The RRF for each target analyte must vary by no more than 25% from the average RRF for that analyte from the associated IC (Percent Difference, %D,  $\leq 25\%$ )<sup>3</sup>.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, if any of the above criteria are not met, sample analysis must be stopped, appropriate corrective action must be taken and documented, and the following actions must be taken:

- The affected run(s) may be repeated once; if acceptable results are obtained, sample analyses may continue.
- If the criteria are not met after the repeated calibration analysis, then (1) all samples run since the last "in control" CC must be re-analyzed; and (2) a new initial calibration; must be established on the instrument.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, an acceptable CC is mandatory before sample analysis may proceed.

#### 6.5.1.4 Ending Calibration

Unless otherwise specified in the PQAP or in the method specified in the PQAP, a second mid-range calibration standard must be analyzed at the end of each 12-hour analysis shift to confirm that the instrument response has remained sufficiently stable over the analysis period to produce reliable qualitative and quantitative results for all of the samples analyzed. All sample analyses must be "bracketed" by a successful calibration standard run at the beginning of the analysis period and another successful calibration standard run at the end of the analysis period. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements shall apply:

- Immediately after the last sample has been injected, another mid-level calibration standard shall be run. "Immediately" shall be interpreted to mean that injection of the shift-ending standard must take place within one (1) hour of the completion of the last sample analysis.
- A successful shift-ending calibration standard may be used to start a new 12-hour analysis shift only if a new tuning compound run is performed prior to its injection; the one hour time limit specified above must still be met.
- If sample analysis is terminated sooner than 12 hours after injection of the tuning compound, a shift-ending calibration standard must be run immediately after the last sample run is completed.
- Four compounds are permitted to be outside  $\leq 25\%D$  quality control limit provided the results are  $\leq 50\%D$ .
- Any variations from the above requirements must be approved by DNREC.

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<sup>3</sup> If the PQAP specifically permits the use of linear regression or another type of calibration curve, and one was used for one or more compounds, the percent difference must be based on the measured value of the compound in the CC standard and the known value of the standard:

$$100 \times \frac{\text{true value} - \text{measured value}}{\text{true value}}$$

## 6.5.2 GC Calibration

Calibration allows generation of quantitative results according to specific procedures on a particular instrument; QC criteria defining satisfactory initial calibration are designed and monitored to ensure that the instrument is capable of producing acceptable (i.e., consistent and accurate) results for that method under the current conditions. QC criteria defining satisfactory continuing and ending calibrations are designed and monitored to ensure that instrument responses remain consistent enough to allow accurate qualitative and quantitative evaluation of sample results during the current analysis shift.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, following are several requirements that are generally applicable to all GC methods performed for the State of Delaware:

- All samples and method blanks shall be analyzed on two (2) separate columns, referred to as “primary and secondary” or as “quantitation and confirmation.” GC/MS may be substituted for secondary confirmation. GC confirmation is unnecessary if the results on the primary column are reported not detected and all QC criteria as established in the PQAP have been met.
- All requirements for calibration, instrument performance, quality control, and sample analysis apply to both the primary and secondary column analyses.
- Injection volumes must be identical for all standards, samples, and blanks analyzed under an initial calibration.

### 6.5.2.1 Initial Calibration

Initial calibration establishes that an instrument is capable of acceptable performance at the start of the analyses.

#### 6.5.2.1.1 Initial Calibration Specifications

Initial calibration (IC), or demonstration of linearity of response, shall be performed for all GC methods as prescribed in the selected analytical method with respect to required standard concentrations, the specific analytes to be calibrated, and the required sequence of analyses. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements shall apply to initial calibrations for all GC analyses performed in support of projects for the State of Delaware.

- An IC shall be performed on every instrument used to analyze samples.
- An IC must be established (or re-established) on every instrument:
  - prior to any sample analyses;
  - whenever a new column is installed;
  - whenever instrument adjustments that affect sensitivity are made;
  - whenever continuing calibration standard does not meet specified acceptance criteria; and
  - whenever the selected method has not been performed on that instrument for more than 30 calendar days.
- The IC must be comprised of an instrument blank (IB) and a minimum of three (3) standard concentration levels. An instrument blank is a volume of the extraction solvent spiked with the method-specified surrogate compounds. Within a batch, all IB's must be uniquely

identified; IB01, IB02, IB02, (etc.) shall be used as the “EPA Sample Numbers” for IB’s run and reported in a single batch for any GC analysis. For volatiles in water analysis, the instrument blank is equivalent to a method blank, and does not need to be run in addition to the method blank.

- The Calibration Factor (CF) for each individual analyte at each concentration level shall be calculated as the amount injected ( g) divided by the peak area response as measured by the data system.
- If the data system incorrectly integrates a peak, then a manual integration shall be performed and documented: the chromatogram must show the manually drawn baseline and any verticals used, and the manual area/height must be written on the quantitation report, next to the automatic area it replaces. An “M” must be appended to all manual areas used for quantitation.
- The CF for each standard level, the average CF, and the percent relative standard deviation (% RSD) shall be documented on , Initial Chromatographic Calibration, or a similar form; all of the indicated information must be provided on the form used.

#### 6.5.2.1.2 Initial Calibration Acceptability Criteria

Unless otherwise specified in the PQAP or in the method specified in the PQAP, an acceptable IC will meet the following criteria:

- The instrument blank is acceptable, i.e., no peaks are detected at the retention time for any target analyte;
- All analytes are detected at all levels; and
- The %RSD for each analyte CF is  $\leq 20$  (or lower, if so specified by the selected method).

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***Note: Unless otherwise specified in the PQAP or in the method specified in the PQAP, the use of linear regression or other calibration curves in lieu of use of mean CFs is NOT acceptable to DNREC.***

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Unless otherwise specified in the PQAP or in the method specified in the PQAP, if the above criteria are not met following analysis of the series of IC standards, then the following actions shall be taken:

- If a bad injection or instrument malfunction is suspected, then the affected standard(s) shall be re-analyzed; acceptable standard runs for all IC levels must be generated within a maximum time period of 12 hours.
- The working calibration standard solutions should be checked (by separate injection on a different instrument) to determine if degradation, concentration, or contamination has occurred.
- Appropriate corrective action, as determined by the laboratory, shall be taken and documented.
- The IC sequence must be repeated until acceptable results are obtained.

An acceptable IC is mandatory before sample analysis may proceed.

### 6.5.2.2 Instrument Performance

Instrument performance criteria have been established for the analysis of pesticides/PCBs in the USEPA method described in the current version of the CLP SOW. These address both qualitative and quantitative performance, and must be met as part of the initial calibration (as well as in subsequent continuing calibration checks, as described in Section 6.5.2.3), and are intended to ensure that chromatographic resolution and sensitivity are sufficient to obtain valid results.

Where applicable, similar instrument performance criteria are required as described below for other parameters analyzed by GC methods.

#### 6.5.2.2.1 Demonstration of Resolution

Resolution is a measure of the separation between two (2) closely eluting peaks in a chromatogram. Since analyte identifications are based entirely on retention times in GC methods, it is imperative that individual analytes be sufficiently resolved to be able to distinguish between them on this basis alone.

##### 6.5.2.2.1.1 Pesticide/PCB Analysis

Unless otherwise specified in the PQAP or in the method specified in the PQAP, a “Resolution Check Mixture” consisting of the compounds listed below (at the indicated concentrations) shall be prepared as prescribed in the CLP SOW method:

<i>Compound</i>	<i>Concentration (ng/mL)</i>
gamma-Chlordane	10.0
Endosulfan I	10.0
4,4'-DDE	20.0
Dieldrin	20.0
Endosulfan Sulfate	20.0
Endrin ketone	20.0
Methoxychlor	100.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

This shall be the first analysis of an initial calibration sequence. The resolution criterion, defined as the depth of the valley between adjacent peaks divided by the height of the shorter of the adjacent peaks, must be  $\leq 60\%$  between all adjacent peaks.

The resolution criterion between all adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the IC for pesticide/PCB analysis must be  $\geq 90\%$ , i.e., the height of the valley between adjacent peaks must be  $\leq 10\%$  of the smaller peak.

A “Performance Evaluation Mixture” containing the following compounds at the indicated concentrations shall be prepared as prescribed by the CLP SOW method:

<i>Compound</i>	<i>Concentration (ng/mL)</i>
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gamma-BHC	10.0
alpha-BHC	10.0
4,4'-DDT	100.0
beta-BHC	10.0
Endrin	50.0
Methoxychlor	250.0
Tetrachloro-m-xylene	20.0
Decachlorobiphenyl	20.0

The Performance Evaluation Mixture is the second analysis in the initial calibration sequence for pesticide/PCB as well as the last analysis performed in the IC sequence prior to sample analysis. All pairs of adjacent peaks must be 100% baseline resolved in both of these analyses.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, if any of the resolution criteria described above are not met during the initial calibration for pesticide/PCB analysis, then corrective action must be taken, and the initial calibration sequence must be repeated. All resolution criteria must be met before any samples or blanks are analyzed.

#### 6.5.2.2.1.2 Other Parameters

For other parameters analyzed by GC, unless otherwise specified in the PQAP or in the method specified in the PQAP, adequate resolution between standard peaks must be demonstrated in the mid-level concentration standard during initial calibration. The resolution criterion shall not exceed 75% between any pair of adjacent peaks.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, if the resolution criterion is not met during the initial calibration, then corrective action must be taken and the initial calibration must be repeated. The resolution criterion must be met before any samples or blanks are analyzed.

#### 6.5.2.2.2 Retention Time Window

Qualitative identification of target analytes by GC analysis is entirely dependent on the matching of retention times between calibration standards and samples. It is imperative, therefore, that retention times be closely monitored from run to run, and that retention time shifts be kept to an absolute minimum.

##### 6.5.2.2.2.1 Pesticide/PCB Analysis

An average retention time (RT) is calculated for each single component pesticide from the absolute RT for that analyte in the three (3) analyses of the Individual A and B Mixtures during initial calibration. Absolute and average RT's are documented on CLP Form VI PEST-1, -2 or equivalent, Initial Chromatographic Calibration of Single Component Analytes.

For multicomponent analytes, the RT's for each of 3-5 individual peaks from each IC standard are recorded on CLP Form VI PEST-3 or equivalent, Initial Chromatographic Calibration of Multicomponent Analytes. Unless otherwise specified in the PQAP or in the method specified in the PQAP, at least three peaks are required to identify and quantify multicomponent analytes.

The precision of the absolute RT's for each individual analyte in each of the three initial calibration standards will be a measure of the confidence by which a compound of concern can

be identified. Unless otherwise specified in the PQAP or in the method specified in the PQAP, retention time windows for each single component pesticide and for each of the selected peaks for each multicomponent analyte are defined as  $\pm 0.07$  or  $\pm .10$  minutes from the average retention time except as indicated in the most current EPA CLP statement of work.

#### 6.5.2.2.2 Other Parameters

For other parameters analyzed by GC methods, RT windows shall be established as part of the initial calibration. For each individual analyte, the absolute RT from each initial calibration standard shall be recorded on CLP Form VI PEST or equivalent, Initial Chromatographic Calibration; the average RT is then calculated and recorded. The RT window is defined as the average RT  $\pm$  three (3) times the standard deviation of the absolute RT's. The RT windows must be re-established every time a new initial calibration is performed.

#### 6.5.2.2.3 DDT/Endrin Breakdown

DDT and Endrin breakdown criteria are specific to the analysis of pesticides/PCB's. As part of the initial calibration criteria, breakdown must be calculated in both of the Performance Evaluation Mixture runs, as specified in the CLP SOW method or as stipulated in the referenced method.. Unless otherwise specified in the PQAP or in the method specified in the PQAP, individual breakdown values must be  $< 20\%$ , and the combined breakdown for DDT and endrin must be  $< 30$  percent.

Breakdown of DDT and Endrin will be calculated according to the following equation:

$$\% \text{ Breakdown DDT} = \frac{\text{Amount found in ng (DDD + DDE)} * 100}{\text{Amount in ng of DDT injected}}$$

$$\% \text{ Breakdown Endrin} = \frac{\text{Amount found in ng (Endrin aldehyde + Endrin ketone)} * 100}{\text{Amount in ng of Endrin injected}}$$

If breakdown criteria are not met in the initial calibration sequence, then appropriate corrective action must be taken and the initial calibration must be repeated. Analysis of samples cannot proceed until acceptable breakdown levels are achieved.

Breakdown calculation results must be reported on CLP Form VII PEST or equivalent, Pesticide Calibration Verification Summary.

#### 6.5.2.3 Continuing Calibration

Once the IC is successfully established on an instrument, sample analyses may begin. Continuing Calibration standard checks are performed at regular intervals to ensure that instrument responses remain sufficiently consistent to allow accurate qualitative and quantitative evaluation of sample results.

##### 6.5.2.3.1 Continuing Calibration Specifications

Continuing calibration (CC) standards at or near the mid-point of the IC range shall be prepared and run for all GC methods as prescribed in the selected analytical method. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements shall apply to continuing calibrations for all GC methods performed in support of projects for DNREC.

- A CC shall be performed, at a minimum, at the start of every 12-hour shift on every instrument on which samples are analyzed.
- The CC shall include, at a minimum, an instrument blank run followed by a calibration standard run; the calibration standard shall be at or near the mid-point concentration of the IC range.
- The 12-hour shift begins when the instrument blank is injected. Samples may be injected until 12 hours have elapsed on the system clock.
- For pesticide/PCB analysis (CLP SOW), every other 12-hour period is begun
- with analysis of an instrument blank and the mid-level Individual Standard Mixtures A and B. The alternating 12-hour periods are begun with analysis of an instrument blank and the Performance Evaluation Mixture. All sample analyses must be bracketed by instrument blank and Individual A/B standard runs at one end, and instrument blank and Performance Evaluation Mixture runs at the other end of the 12-hour analysis shift or as stipulated in the referenced method.
- For pesticide/PCB analysis (CLP SOW), if more than 12 hours have elapsed since
- the end of the previous 12-hour period, then an instrument blank and Performance Evaluation Mixture must be injected to start a new 12-hour analysis period under the existing IC, no matter what was run at the end of the last 12-hour period.

#### 6.5.2.3.2 Continuing Calibration Acceptability Criteria

Unless otherwise specified in the PQAP or in the method specified in the PQAP, an acceptable CC for all analyses other than pesticides/PCB's will meet the following criteria:

- In the instrument blank analysis at the start and end of a 12-hour analyses period, no peaks are detected and the retention time for any target analyte and the surrogate retention times are within the RT windows.
- In the calibration standard, the retention time for each calibrated analyte must be within the RT window from initial calibration.
- The resolution criterion between any two adjacent peaks must be  $\geq 75\%$ .
- The percent difference (%D) between the CF for each analyte in the CC and the average CF from Initial calibration must be  $\leq 25\%$ .

For pesticide/PCB analysis, unless otherwise specified in the PQAP or in the method specified in the PQAP, the following criteria shall apply (as specified in CLP SOW).

- All instrument blanks must meet the acceptance criteria specified above.
- The absolute RT for each single component pesticide and surrogate in the Performance Evaluation Mixtures and the Individual Standard Mixtures must be within  $\pm 0.02$  minutes of the mean RT from initial calibration; for methoxychlor, the RT window is  $\pm 0.025$  minutes.
- The relative percent difference (RPD) of the calculated amount and the true amount for each single component pesticide and surrogate in the Performance Evaluation Mixtures and Individual Standard Mixtures must be  $\leq 25\%$ .

- The percent breakdown for DDT and Endrin in the Performance Evaluation Mixture must be  $\leq 20\%$  on both columns; the combined breakdown must be  $\leq 30\%$  on both columns.

If any of the criteria described above (for any analysis parameter) are not met, then sample analysis must be stopped, appropriate corrective action taken and documented, and the following actions taken:

- The affected run may be repeated once; if acceptable results are obtained, sample analysis may continue.
- If the criteria are not met after the repeated calibration analysis, then (1) all samples run since the last “in control” CC must be re-analyzed; and (2) a new initial calibration must be established on that instrument.

Verification of continuing calibration acceptability shall be summarized on CLP Form VII PEST or equivalent, Pesticide Continuing Calibration Verification Summary.

#### **6.5.2.4 Ending Calibration**

Unless otherwise specified in the PQAP or in the method specified in the PQAP, a second mid-range calibration standard must be analyzed at the end of each 12-hour analysis shift to confirm that the instrument response has remained sufficiently stable over the analysis period to produce reliable qualitative and quantitative results for all of the samples analyzed. All sample analyses must be “bracketed” by a successful calibration standard run at the beginning of the analysis period, and another successful calibration standard run at the end of the analysis period. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the following requirements shall apply:

- Immediately after the last sample has been injected, another instrument blank and mid-level calibration standard shall be run. “Immediately” shall be interpreted to mean that injection of both the ending IB and the ending CC must take place within one (1) hour of the completion of the last sample analysis.
- The instrument blank and calibration standard ending a 12-hour period may also be used to start the next 12-hour period.
- If more than 12 hours have elapsed since the injection of the instrument blank and standard ending the previous 12-hour period, then a new instrument blank and calibration standard must be injected to start a new 12-hour analysis period under the existing IC.
- If sample analysis is terminated sooner than 12 hours after injection of the initial instrument blank, an ending instrument blank and mid-level calibration standard must be run immediately after the last sample run is completed.

#### **6.5.2.5 Cleanup Procedures**

Unless otherwise specified in the PQAP or in the method specified in the PQAP, all cleanup procedures (e.g., GPC, florosil, sulfur cleanup, etc.) are optional, regardless of matrix, on all semivolatile and Pesticide/PCB extracts with the following exceptions:

- the semivolatile extracts for non-aqueous media are not diluted by more than a factor of five due to matrix interference:

- the Pesticide/PCB practical quantitation limits in non-aqueous media are below the following levels shown in Table 6-8.

Please note: Unless otherwise specified in the PQAP or in the method specified in the PQAP, pesticide in non-aqueous media can be analyzed by GC/MS provided the practical quantitation limits shown in Table 6-8 are not exceeded.

#### **6.5.2.6 PCB Only Analysis Sequence**

Unless otherwise specified in the PQAP or in the method specified in the PQAP, PCB's will require the following calibration sequence:

1. An instrument blank and a five point initial calibration with any one Arochlor will be utilized with a RSD of 20%.
2. The remaining Arochlors will be analyzed as single point calibration.
3. Sample analysis can immediately proceed following a compliant initial calibration.
4. All samples will be bracketed with a compliant continuing calibration every ten samples.
5. A continuing calibration must be within  $\pm 25\%$  of the initial calibration.
6. Samples must be reanalyzed under a new sequence if not bracketed by a compliant continuing calibration.
7. If the analysis determines the presence of an Arochlor other than the one utilized in the initial five point calibration, then a new initial calibration must be established with the identified Arochlor and the sequence must be repeated without the remaining Arochlors.
8. The blank spike, matrix spike and matrix spike duplicate will be spiked with any Arochlor at approximately three to five times the practical quantitation limit (See current CLP SOW for PQL).

#### **6.5.3 ICP and AA Calibration**

##### **6.5.3.1 Initial Calibration**

Initial instrumental calibration for ICP and AA analyses will be conducted daily or every twelve (12) hours of operation whichever is more frequent. Calibration results will be reported on CLP Form 2 or equivalent.

##### **6.5.3.1.1 ICP**

Initial calibration of an ICP will consist of the analysis of a blank and a standard calibration solution. The concentration of the standard solution will be chosen to be higher than the anticipated highest concentration in any sample but not higher than the linear range of the instrument. The response of the instrument will be assumed to be linear in the range between the blank and the concentration of the daily calibration standard.

##### **6.5.3.1.2 Atomic Absorption**

The linear range of the instrument will be determined by analyzing a series of calibration standards and plotting the instrument response against the standard concentrations. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the correlation coefficient of the regression line for at least three points must be equal to or greater than 0.995 to define the linear range of the instrument. The linear range must be bounded by calibration standards actually analyzed; unless otherwise specified in the PQAP or in the method specified

in the PQAP, extrapolations of regression lines are not permitted. Unless otherwise specified in the PQAP or in the method specified in the PQAP, instrument manufacturers' specifications for instrumental linear range are not an acceptable substitute for determining the linear range of an instrument.

### **6.5.3.2 Calibration Verification**

#### **6.5.3.2.1 Initial Calibration Verification**

Immediately after initial calibration of an instrument, the calibration of the instrument will be verified by analysis of a standard solution from a source independent of the initial calibration standard. The verification standard concentration must have been determined by an external laboratory and must have documented evidence of its concentration. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the instrument response for the verification standard must agree within 10% of the known concentration in order to consider the instrument properly calibrated. If the agreement is outside of the specified window, the instrument must be recalibrated, possibly with different initial calibration standards, until the verification standard response is within the specified limits.

Unless otherwise specified in the PQAP or in the method specified in the PQAP, if the verification standard response is outside of the specified window, the standard may be re-injected. However, a satisfactory response on the second injection may not be taken as an indication that the instrument is within calibration limits. The evidence at hand is that, on two injections, one is in control and one is out of control. There is no reason to expect that one of the results is any more valid than the other. Consequently, once a verification standard has failed to respond within the limits, sufficient re-injections must be analyzed to provide confidence that the response outside of the specified limits was, in fact, a momentary excursion.

#### **6.5.3.2.2 Continuing Calibration Verification**

After the calibration of the instrument has been verified, analyses of QC standards, QC samples, and field samples may begin. Unless otherwise specified in the PQAP or in the method specified in the PQAP, continuing calibration verification standard must be analyzed after every ten (10) injections which include QC standards, QC samples and field samples. Unless otherwise specified in the PQAP or in the method specified in the PQAP, the instrument response for the verification standard must agree within 10% of the known concentration in order to consider the instrument still in calibration. If the agreement is outside of the specified window, analyses must cease, and the instrument must be recalibrated. All samples since the last good verification standard must be reanalyzed.

If the verification standard response is outside of the specified window, it may be re-injected. However, a satisfactory response on the second injection may not be taken as an indication that the instrument is within calibration limits. The evidence at hand is that, on two injections, one is in control and one is out of control. There is no reason to expect that one of the results is any more valid than the other. Consequently, once a verification standard has failed to respond within the limits, sufficient re-injections must be analyzed to provide confidence that the response outside of the specified limits was, in fact, a momentary excursion.

Calibration verification results will be tabulated on CLP Form 2 or equivalent

## 6.6 Analyses of Samples

### 6.6.1 GC/MS Analyses

Unless the PQAP specifies otherwise, the following sections specify the minimum QC requirements for the analysis of samples (or sample extracts) by GC/MS.

#### 6.6.1.1 *Internal Standards*

Internal Standard (IS) compounds are added to every standard, sample, and method blank analyzed for volatiles and semivolatiles by GC/MS only. IS areas are used for quantification of all sample results; also, qualitative identification of target compounds is based in part on retention times relative to the IS retention time. Performance criteria for IS retention times and areas are monitored to ensure that GC/MS sensitivity and response remains stable during every run.

##### 6.6.1.1.1 Specifications

IS compounds are added to all samples, standards, and MB's immediately prior to analysis (to the sample and method blank extracts, in the case of semivolatiles and volatiles in soil). Table 6-9, Internal Standard Specifications, identifies the IS compounds for each fraction and the required spiking levels, unless otherwise specified in the PQAP or in the method specified in the PQAP.

##### 6.6.1.1.2 Acceptability Criteria

IS retention times and areas must be evaluated during or immediately after data acquisition of each analysis run to determine acceptability of the results. Unless the PQAP specifies otherwise, for each run to be acceptable, the following criteria must be met:

- IS retention times in each method blank, sample, or shift-ending CC standard must vary by no more than 30 seconds from the IS retention times in the successful continuing calibration standard on that instrument run at the start of the 12-hour shift.
- The Percent Relative Standard Deviation (%RSD) of the areas for each IS in the five (5) IC standards must be  $\leq 30\%$ .
- IS areas in the successful continuing calibration standard at the start of a 12-hour shift must vary by no more than a factor of 2 in either direction (-50% to +100%) from the average of the IS areas in the five (5) initial calibration standard runs. The beginning continuing calibration standard must meet this requirement before sample analyses proceed on that instrument under that 12-hour shift.
- IS areas in each method blank or sample and the shift-ending CC standard must vary by no more than a factor of 2 in either direction (-50% to +100%) from the IS areas in the successful continuing calibration standard on that instrument run at the start of the 12-hour shift.

##### 6.6.1.1.3 Actions Required Based on IS Response

If the IS responses for all continuing calibration standards, samples and MB's for volatiles and semivolatiles in an analysis batch are within the acceptability criteria specified in Section 6.6.1.1.2, then no action is required and sample processing may proceed.

Unless the PQAP specifies otherwise, if any IS area or retention time in the beginning continuing calibration standard, any sample, or any method blank does not meet the criteria specified in Section 6.6.1.1.2, then the following actions must be taken in the order specified:

- Check the integrity of the IS spiking solution by injection on a different successfully tuned and calibrated instrument. Results of this injection must be documented in the data package as described in Section 7. If degradation or contamination of the solution is confirmed, then all affected standards or samples must be re-analyzed using a new IS solution.
- If the integrity of the IS solution is confirmed, then all affected samples must be re-extracted and/or re-analyzed.
- A sample matrix effect cannot be concluded on the basis of a re-injection of the original extract; re-extraction of the sample, using a confirmed IS solution, is mandatory under the circumstances described above.

Unless the PQAP specifies otherwise, if any IS area or RT in the shift-ending CC standard does not meet the criterion specified in Section 6.6.1.1.2, then the following actions must be taken:

- All samples and MB's analyzed on that shift (i.e., since the successful beginning CC standard) must be re-analyzed under a new calibration.
- The unsuccessful shift-ending CC standard may not be used to begin a new 12-hour analysis shift.

#### 6.6.1.1.4 Additional IS Requirements for Method Blanks

Unless the PQAP specifies otherwise, method blanks must generate IS responses that meet the specified criteria; since no matrix effects are possible, any deviation must be due to problems within the laboratory's control. For volatiles, sample analyses shall not proceed on any 12-hour shift until a method blank with acceptable IS responses are analyzed following the successful tune and calibration. For semivolatiles, all samples associated with the affected distilled water method blank must be re-extracted and/or re-analyzed after successful corrective action has been taken and documented.

#### 6.6.1.1.5 Documentation

IS retention time and areas shall be reported on the Internal Standard Area and RT Summary (CLP Form 8 or equivalent) for all standards (initial and continuing calibration), MB's and samples analyzed for volatiles or semivolatiles by GC/MS.

### 6.6.1.2 Sample Analyses

The term "sample" includes field samples, method blanks, and MS/MSD's. Sample analyses may be performed only after successful instrument performance (tuning) and calibration (initial and continuing) is demonstrated, as described above. Unless the PQAP specifies otherwise, sample analysis (i.e., injection of a sample) may continue until 12 hours have elapsed on the system clock from the injection time of the tuning compound run at the start of the analysis period. In other words, if the tuning compound was injected at 07:30, then samples may be injected until the system clock reads 19:30, injection of a sample at 19:45 in this example would not be acceptable. The shift ending calibration standard in this example must be injected no later than 20:30 plus the run time of the last sample, assuming the last sample was injected at

precisely 19:30. Results for samples run under any other circumstances will not be technically correct or legally defensible.

#### **6.6.1.2.1 Run Sequence and Documentation**

Unless the PQAP specifies otherwise, the sequence of sample and supporting standard, blank, and tuning compound analyses must be performed as described above. The 12-hour period in which an IC is performed may also be used to analyze samples, provided that a method blank is run after the last standard and before any samples; the time limit for injecting samples is identical to that described for a period in which a CC standard is run, and a shift-ending calibration standard must still be run.

Immediately following a sample run in which one or more analytes exceeded the calibration range of the instrument an IB (see Section 6.4.2.1.1) shall be run to confirm that carry-over is not a problem. The IB must be reported in the data package, as described in Section 7. If an autosampler is used, then the runs immediately following the high level sample must be evaluated for carry-over; if the affected compound(s) are detected, the samples must be re-analyzed.

The actual analyses performed on an instrument, in chronological order, shall be recorded in the Instrument Run Log, which must contain, at a minimum, the information illustrated. It is not necessary that this exact format be used, but it is essential that all of the indicated information be supplied.

#### **6.6.1.2.2 Qualitative Analyte Identifications**

Qualitative identification of a target analyte is established based on two criteria: (1) elution of the sample component at the same relative retention time (RRT) as the standard component; and (2) correspondence of the sample and standard mass spectra for this component.

Unless the PQAP specifies otherwise, requirements for matching RRT's and mass spectra as described in the CLP SOW must be followed. In particular, the following items are emphasized:

- Spectra comparisons must be performed by an analyst experienced and competent in the interpretation of mass spectra for the target parameters; and
- If, in the judgment of the analyst, a spectrum fails to meet all of the ion-matching criteria only because it is present at a very low level in the sample, then the component shall be reported.

#### **6.6.1.2.3 Quantitation of Identified Analytes**

Formulas for quantitation of identified analytes are dependent on the specifics of the method being used; therefore, quantitations must be performed according to the formulas specified in the selected method. Unless the PQAP specifies otherwise, the following general quantitation requirements shall apply to all GC/MS analyses performed for the State of Delaware:

- Quantitation must be performed by the method of internal standards.
- Quantitation of an analyte is performed using the RRF from the continuing calibration standard run at the start of the 12-hour period in which the sample was analyzed.

- If samples are analyzed during the same 12-hour period in which an IC is run, sample quantitations are performed using the RRF's from the mid-level IC standard.
- When manual integration of a peak in a sample run is necessary, it must be documented as described above (Section 6.5.2.1.1).
- When the RRF for an analyte is calculated using a manually integrated area, any sample results for that analyte must be calculated in an identical manner; i.e., the analyst must take care to ensure that the sample peak is integrated (baseline, vertical placements) for the same ion in the same manner as was the standard peak.

#### 6.6.1.2.4 Tentatively Identified Compounds (TIC's)

Unless the PQAP specifies otherwise, extraneous (non-target compound, non-internal standard, non-surrogate) peaks shall be evaluated for all GC/MS methods. The number of extraneous peaks to be reported (as "Tentatively Identified Compounds", or TIC's), the minimum size requirements for evaluation of an extraneous peak, and calculation of the estimated concentration will be defined by the selected method.

Unless the PQAP specifies otherwise, the following additional requirements shall apply to TIC's reported from analyses performed for the State of Delaware:

- All visible extraneous peaks in the method blanks shall be library searched and reported, regardless of peak height in comparison to the nearest internal standard.
- Volatile target analytes shall not be reported as TIC's in the semivolatile fraction, however, if the peak is large enough to warrant evaluation then the library search results shall be included in the data package to document the peak's identification.
- Semivolatile target analytes shall not be reported as TIC's in the volatile fraction, however, if the peak is large enough to warrant evaluation, then the library search results shall be included in the data package to document the peak's identification.
- Any and all TIC's reported in a sample that are also observed in the method blank run on the same analysis shift shall be reported with a "B" qualifier on the estimated concentration.

#### 6.6.1.2.5 Dilution Requirements

Unless the PQAP specifies otherwise, if one or more target analytes in a sample are detected at a level above the concentration of the highest level standard run during initial calibration, then the sample must be rerun at a dilution to achieve a detector response for the affected analyte(s) within the linear range.

A dilution shall be routinely but not exclusively defined as the preparation and analysis of a smaller aliquot of the original sample. If insufficient sample remains to allow re-extraction, or if the holding time has been significantly exceeded, then the original extract may be diluted and re-analyzed.

If the results of a diluted sample analysis do not show a response for one or more analyte peaks above the mid-point of the initial calibration range, then the sample must be rerun using a smaller dilution factor.

Original and dilution results shall be reported for all samples where a dilution was performed. If more than one dilution run is necessary, then only the dilution showing responses above the midpoint of the initial calibration range must be reported with the original results.

Diluted sample results shall be identified and reported as the original field sample number ("EPA Sample Number") with a suffix of "DL."

## **6.6.2 GC Analyses**

The term "sample" includes field samples, method blanks, and MS/MSD's. Unless the PQAP specifies otherwise, sample analyses may be performed only after successful calibration (initial and continuing) is demonstrated, as described above. Sample analysis (i.e., injection of a sample) may continue until 12 hours have elapsed from the injection time of the instrument blank at the start of the analysis period (i.e., if the beginning IB was injected at 08:00, then samples may be injected until the system clock reads 20:00; injection of a sample at 20:05 in this example would not be acceptable).

### **6.6.2.1 Run Sequence and Documentation**

The sequence of sample and supporting standard and blank analyses must be performed as described above, unless the PQAP specifies otherwise.

Immediately following a sample run in which one or more analytes exceeded the calibration range of the instrument, an IB (see Section 6.5.2.1.1) shall be run to confirm that carry-over is not a problem. The IB must be reported in the data package, as described in Section 7. If an autosampler is used, then the run immediately after the high level sample must be evaluated for carry-over; if the affected compound(s) are detected, the sample must be re-analyzed.

The actual analyses performed on an instrument, in chronological order, shall be recorded in the Instrument Run Log, which must contain, at a minimum, the information illustrated. It is not necessary that this exact format be used but it is essential that all of the indicated information be supplied.

### **6.6.2.2 Primary and Secondary Column Analyses**

Unless the PQAP specifies otherwise, all samples must be analyzed on both a primary and secondary column. The target analytes for the method must elute in a different order on the two columns. All criteria for resolution, calibration, retention time windows, and breakdown (pesticide/PCB analysis only) must be met on both columns.

### **6.6.2.3 Qualitative Analyte Identifications**

Qualitative identification of a single component analyte is confirmed and reported when a peak is detected in the established RT window on both the primary and secondary columns.

For multicomponent analytes, pattern recognition on both columns by an experienced analyst is the primary basis for qualitative identifications. In addition, the RT's for the 3-5 peaks documented in initial calibration must be compared to the RT's for the corresponding peaks in the sample chromatograms, and a standard run of the tentatively identified component must be performed on the same instrument within 72 hours of its detection in a sample. This latter requirement may be met by the initial calibration run if less than 72 hours have passed since its injection or as stipulated in the reference method.

Unless the PQAP specifies otherwise, sample chromatograms must adhere to the following requirements:

- All non-solvent peaks in the chromatograms must be on-scale.
- The chromatograms must display the largest non-solvent peak detected in the sample at less than full scale but at least 75% of full scale.
- If possible, the chromatograms should be normalized to the largest non-solvent peak in the sample.
- If no analytes are identified in a sample, the chromatograms must be displayed using the same scaling factor as was used for the low-level standard in the initial calibration.
- If a chromatogram is replotted electronically to satisfy any of these requirements, then both the originally generated chromatogram and the replotted chromatogram must be included in the data package. The adjustments used to generate the replotted chromatogram must be clearly recorded on the chromatogram.
- The surrogate peaks must be accurately labeled on every sample chromatogram.

#### **6.6.2.4    *Quantitation of Identified Analytes***

Formulas for quantitation of identified analytes are dependent on the specifics of the method being used; therefore, quantitations must be performed according to specified formulas. Unless the PQAP specifies otherwise, the following general quantitation requirements shall apply to all GC analyses performed for the State of Delaware:

- Quantitation must be performed for sample results from both column analyses.
- Quantitation of an individual analyte is performed using the CF from the mid-level calibration standard run during the same 12-hour period as the sample.
- For multicomponent analytes, quantitation is performed using the CF from the associated initial calibration.
- Analyte results may be quantitated on the basis of peak area OR peak height, provided the CF from the associated calibration standard has been generated in the same manner.
- When manual integration of a peak in a sample run is necessary, it must be documented as described above (Section 6.5.2.1.1).
- When the CF for an analyte is calculated using a manually integrated area, any sample results for that analyte must be calculated in an identical manner; i.e., the analyst must take care to ensure that the sample peak is integrated (baseline, vertical placements) in the same manner as was the standard peak.

#### **6.6.2.5    *Dilution Requirements***

Unless the PQAP specifies otherwise, if one or more target analytes in a sample are detected at a level above the concentration of the highest level standard run during initial calibration, then the sample must be rerun at a dilution to achieve a detector response for the affected analyte(s) within the linear range.

A dilution shall be routinely defined as the preparation and analysis of a smaller aliquot of the original sample. If insufficient sample remains to allow re-extraction, or if the holding time has been significantly exceeded, then the original extract may be diluted and re-analyzed.

If the results of a diluted sample analysis do not show a response for one or more analyte peaks above the mid-point of the initial calibration range, then the sample must be rerun using a smaller dilution factor.

Original and dilution results shall be reported for all samples where a dilution was performed. If more than one dilution run is necessary, then only the dilution showing responses above the midpoint of the initial calibration range must be reported with the original results.

Diluted sample results shall be identified and reported as the original field sample number ("EPA Sample Number") with a suffix of "D."

### **6.6.3 Inductively Coupled Plasma (ICP) Analyses**

#### **6.6.3.1 Run Sequence**

The run sequence used for ICP analyses involves the interspersing of QC samples with field samples to monitor instrument performance as well as providing data on precision and accuracy of the measurements. The relatively short time of only a few minutes required for the processing of each injection is an advantage in that calibration and system performance can be monitored while maintaining a high throughput of field samples.

Unless the PQAP specifies otherwise, the following run sequence will be used when analyzing samples by ICP:

- Initial calibration (blank and high standard)
- Initial calibration verification standard
- Initial calibration blank
- Interference check sample A
- Interference check sample AB
- Initial Low Level standard
- Method blank
- Laboratory control sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Continuing calibration verification standard 1
- Continuing calibration blank 1
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Field Sample
- Continuing calibration verification standard 2

Continuing calibration blank 2

\*\*\* Sequence of 10 field samples followed by a CCV and a CCB \*\*\*

Field Sample  
Field Sample  
Field Sample matrix spike<sup>†</sup>  
Field Sample duplicate<sup>†</sup>  
Field Sample  
Field Sample  
Field Sample  
Interference check sample A  
Interference check sample AB  
Final Low Level standard  
Final continuing calibration verification standard  
Final continuing calibration blank

#### **6.6.3.2 Low Level Calibration Standard**

The initial and final low level calibration standard indicated in the above sequence are to monitor the ability of the ICP to accurately detect and measure concentrations of metals in the range of the instrument detection limit (IDL). The concentrations of the low level standard should be chosen to be 3 to 5 times the IDL (or two times the CRDL if analyses are being conducted according to EPA Contract Laboratory Program protocols). The instrument response should be within 50% of the true value to be considered acceptable.

#### **6.6.3.3 Interference Check Sample**

Unless the PQAP specifies otherwise or in the method in the PQAP, the instrument response must be within  $\pm 20\%$  of the true value to be considered acceptable. The analytical sequence shall be considered out of control for any analyte outside of quality control limits. Therefore, the analytical sequence must be restarted and samples re-analyzed at the point of the analytical sequence failure for the analyte of interest.

#### **6.6.3.4 Laboratory Control Samples (LCS)**

Unless the PQAP specifies otherwise or in the method of the PQAP, aqueous LCS must be within  $\pm 20\%$  of the true value to be considered acceptable. The preparation and/or analysis shall be considered out of control for any analyte outside of quality control limits. Therefore, the analytical sequence must be restarted for the analyte of interest. Unless the PQAP specifies otherwise, non-aqueous LCS must be within the manufacturers specifications or  $\pm 35\%$  of the true value whichever quality control limit is more stringent. If re-analysis does not rectify the out of control analyte, re-digestion/re-analysis is required.

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<sup>†</sup> The position of the matrix spike and duplicate samples are shown here only to indicate that they must be analyzed in the same analytical batch. They may be analyzed at any time in the run sequence but, preferably, immediately after the field sample that was spiked and duplicated.

#### **6.6.3.5 Matrix Spike Recovery**

Unless the PQAP specifies otherwise or in the method of the PQAP, matrix spike recovery must be within 25% of the true value in order to be considered acceptable. (See Corrective Action Section). If all corrective actions have been implemented, the laboratory may submit matrix spike recovery results outside quality control limits provided the recovery is greater than 30%. The laboratory must redigest and reanalyze all samples associated with poor matrix recovery data. If redigestion and reanalysis do not rectify the problem, then the laboratory will be required to report both sets of data.

Sample results exceeding 4 time the matrix spike concentration will not apply to the above criteria.

#### **6.6.4 Atomic Absorption Analyses**

##### **6.6.4.1 Run Sequence**

The run sequence used for AA analyses involves the interspersing of QC samples with field samples to monitor instrument performance as well as providing data on precision and accuracy of the measurements. The relatively short time of only a few minutes required for the processing of each injection is an advantage in that calibration and system performance can be monitored while maintaining a high throughput of field samples.

The following run sequence will be used when analyzing samples by AA.

- Initial calibration (blank and four standards)
- Initial calibration verification standard
- Initial calibration blank
- Low Level calibration standard
- Method blank
- Laboratory control samples
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Continuing calibration verification standard 1
- Continuing calibration blank 1
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Field Sample
- Field Sample post-digest spike
- Field Sample

Field Sample post-digest spike  
Continuing calibration verification standard 2  
Continuing calibration blank 2

...Sequences of 5 field samples (sample followed by post-digest spike) followed by a CCV and a CCB...

Field Sample  
Field Sample post-digest spike  
Field Sample matrix spike<sup>‡</sup>  
Field Sample duplicate<sup>‡</sup>  
Field Sample duplicate post-digest spike  
Field Sample  
Field Sample post-digest spike  
Field Sample  
Field Sample post-digest spike  
Final continuing calibration verification standard  
Final continuing calibration blank

#### **6.6.4.2 Duplicate Burns**

When analyzing samples by flameless (furnace) AA, duplicate burns must be made. Unless the PQAP specifies otherwise, for positive (i.e., greater than the IDL) responses, the relative standard deviation of the responses from the duplicate burns must be less than 20% to consider the measurement reliable.

#### **6.6.4.3 Post-digest Spikes**

Post-digest spikes must be analyzed immediately after the sample being spiked. The concentration of the spike must be equivalent to 3-5 times the IDL (or as specified by the latest EPA CLP program if those protocols are used). Unless the PQAP specifies otherwise or in the method specified in the PQAP, the spike must be within 15% of the true value to be considered acceptable.

#### **6.6.4.4 Matrix Spike Recovery**

Unless the PQAP specifies otherwise or in the method specified in the PQAP, matrix spike recovery must be within 25% of the true value in order to be considered acceptable. (See Corrective Action Section). If all corrective actions have been implemented, the laboratory may

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<sup>‡</sup> The position of the matrix spike and duplicate samples are shown here only to indicate that they must be analyzed in the same analytical batch. They may be analyzed at any time in the run sequence but, preferentially, immediately after the field sample that was spiked and duplicated. Note that a post-digest spike is not required for the matrix spike but is required for the duplicate. The duplicate sample refers to a laboratory duplicate, not a field duplicate; field duplicates (and blanks) must be processed as routine field samples.

<sup>‡</sup> The position of the matrix spike and duplicate samples are shown here only to indicate that they must be analyzed in the same analytical batch. They may be analyzed at any time in the run sequence but, preferentially, immediately after the field sample that was spiked and duplicated. Note that a post-digest spike is not required for the matrix spike but is required for the duplicate. The duplicate sample refers to a laboratory duplicate, not a field duplicate; field duplicates (and blanks) must be processed as routine field samples.

submit matrix spike recovery results outside quality control limits provided the recovery is greater than 30%. The laboratory must redigest and reanalyze all samples associated with poor matrix recovery data. If redigestion and reanalysis do not rectify the problem, then the laboratory will be required to report both sets of data.

Sample results exceeding 4 time the matrix spike concentration will not apply to the above criteria.

#### **6.6.4.5    *The Low Level Calibration Standard***

The low level calibration standard should be chosen to 3 to 5 times the instrument detection limit. The response should be within 50% of the true value to be considered acceptable.

#### **6.6.4.6    *Laboratory Control Samples (LCS)***

Unless the PQAP specifies otherwise or in the method specified in the PQAP, aqueous LCS must be within  $\pm 20\%$  of the true value to be considered acceptable. The preparation and/or analysis shall be considered out of control for any analyte outside of quality control limits. Therefore, the analytical sequence must be restarted for the analyte of interest. Unless the PQAP specifies otherwise or in the method specified in the PQAP, non-aqueous LCS must be within the manufacturers specifications or  $\pm 35\%$  of the true value whichever quality control limit is more stringent. If re-analysis does not rectify the out of control analyte, re-digestion/re-analysis is required.

#### **6.6.4.7    *Choosing the Appropriate Metals Method***

Traditionally, Arsenic, Lead, Thallium, Selenium, and in some instances, Antimony, are analyzed by AA. Unless the PQAP specifies otherwise, the laboratory may choose to use either ICP or AA provided the practical quantitation limits are below the following levels for soil (non-aqueous) and water (aqueous) media:

<b>Compound</b>	<b>Non-aqueous (mg/Kg)</b>	<b>Aqueous (ug/L)</b>
Arsenic	<10	<10
Lead	<50	<5
Thallium	<10	<10
Selenium	<50	<50
Antimony	<30	<15

### **6.7    Reporting Sample Results**

Sample results must be reported in a clear, consistent manner for all parameters. Unless the PQAP specifies otherwise, the following conventions shall apply for samples analyzed for DNREC.

#### **6.7.1    Documentation**

Final calculated sample results shall be summarized in the Organic Analysis Data Sheets (CLP Form 1), or an equivalent form that contains all of the same information. The "EPA Sample Number" shall be defined as the field sample number (not the lab sample number, if different); the field sample number shall be used to report all sample results on all data reporting forms.

### 6.7.2 Minimum Reportable Levels

Unless the PQAP specifies otherwise, any positive target compound result that meets the qualitative identification criteria (Sections 6.6.2.3 and 6.6.2.4) shall be reported. If the calculated value is below the method detection limit, then the value shall be qualified as estimated (see below).

### 6.7.3 Laboratory-Reported Qualifiers

All results shall be annotated on the Organics Analysis Data Sheet with the following qualifiers, wherever appropriate, by the laboratory:

- U - Indicates compound was analyzed for but not detected. The associated value is the method detection limit or quantitation limit.
- J - Indicates an estimated value; used to flag estimated concentrations of TIC's and to flag positive results that are below the detection limit or quantitation limit.
- N - Indicates presumptive evidence of a compound; used for all TIC's assigned a specific identification based on the library search.
- P - Used to flag a reported pesticide/PCB analyte result when there is > 25% difference between the reported result and the calculated result from the second column analysis.
- C - Indicates that a pesticide/PCB result was qualitatively confirmed (successfully) by GC/MS.
- B - Indicates that the analyte was also detected in the associated method blank; no evaluation of comparative levels is to be made by the laboratory. Used for TIC's and target analytes, only when the sample shows a positive result for that compound.
- E - Indicates that the result for the flagged compound exceeded the calibration range of the instrument; no value is reported with this flag.
- D - Indicates that the reported value was obtained in an analysis performed at a secondary dilution factor.

Other flags may be defined by the laboratory as needed to further define the reported results. If and when used, the laboratory-defined flags must be fully described in the data package, both in the narrative and on the affected Form I's.

### 6.7.4 Significant Figures

Unless the PQAP specifies otherwise, the following will apply:

- All results for GC analytical methods shall be reported to two (2) significant figures.
- All results for GC/MS analytical methods shall be reported to two (2) significant figures if the value is greater than 10, and to one (1) significant figures if the value is less than 10 or as defined good laboratory practice.
- All inorganics analysis results shall be reported to two (2) significant figures for values less than 10 and three (3) significant figures for values equal to or greater than 10.

- Results should be rounded off only after all calculations have been completed, according to the following rules:
  - Values less than 5 are rounded down
  - Values greater than 5 are rounded up
  - Values equal to 5: retained even digit is unchanged; odd digit is rounded up

#### **6.7.5 False Positives**

Values that appear to indicate the presence of a target analyte on the quantitation report for a sample analysis but are determined to be false positives by the analyst shall be documented as follows:

- If the analysis is by GC/MS, the mass spectrum for the falsely identified peak shall be included in the data package, and clearly labeled “false positive.”
- If the peak is large enough, a library search of a false positive in a GC/MS analysis shall be performed and reported in addition to inclusion of the mass spectrum.
- If the analysis is by GC, the entry on the quantitation report shall be noted as “false positive,” with a brief explanation of how that conclusion was reached (e.g., “false +, not confirmed on second column,” or “false +, confirmed by GC/MS to be phthalate”).

#### **6.7.6 Blank Contamination**

Unless the PQAP specifies otherwise, all sample results shall be reported without correction for blank contamination.

Every analyte detected in a sample that was also detected at any level in the associated method blank shall be noted as such by adding “B” to the reported sample result.

#### **6.7.7 Multiple Sample Analyses**

Samples may be analyzed more than once for a variety of reasons. Unless the PQAP specifies otherwise, multiple sample analysis results shall be reported in chronological order; the original analysis results shall always be placed first, for that sample, in the data package.

Unless the PQAP specifies otherwise, the following requirements shall apply with respect to reporting multiple analysis data for a single sample under the specified circumstances.

##### **6.7.7.1 Dilutions**

When dilutions of a sample is required, two (2) sets of results shall be reported, either the screening data and the diluted analysis run, or the original analysis and the successful dilution. If a sample is analyzed at more than one dilution, only the run that contained analytes in the upper half of the calibration range shall be reported with the original data. The “field sample number” for the dilution results shall be the original field sample number with “D” appended.

If only a single analysis, at a dilution, is performed the basis for performing the dilution must be explained in a Narrative to the data package.

##### **6.7.7.2 Re-Analyses and Re-Injections**

An important distinction must be made between re-analyses and re-injections. Re-analysis of

a sample implies that a separate aliquot of a sample (as in a laboratory duplicate analysis) is taken through an entire analytical procedure usually as a result of a discrepancy or question regarding the initial analysis. Re-injections imply repeated introductions of the exact same extract or digestate into a measuring instrument.

Responses from re-injections measure only the ability of the instrument to reproduce a signal whereas responses from re-analyses are a measure of the precision of the entire analytical method. The precision of instrumental responses for a given extract or digestate (re-injections) is usually considerably better than the precision of instrumental responses from separate extracts from two aliquots of the same sample (re-analyses). When reporting analytical results, the precision of the responses from re-injections must not be confused with or implied to be the precision of the measurements for re-analyses.

#### **6.7.7.2.1 Re-Injections**

Since the analysis of a water sample for volatile organic compounds by purge and trap techniques involves a fresh aliquot of sample, re-injection for this type of analysis is not possible. However, when soil samples are analyzed for volatile organic compounds, the samples are first extracted with a solvent. Since only a portion of the solvent solution is used for purging, re-injections can be accomplished by analyzing another portion of the solvent solution.

Similarly, if portions of an original sample extract for any parameter is introduced into an instrument multiple times, the results must be classified as re-injections. The multiple responses shall be reported in the data package as re-injections by appending "RI" to the field sample number.

If multiple re-injections are performed on the same sample, all analysis results shall be reported. Analyses shall be distinguished by appending "RI1," "RI2," "RI3," and so on as necessary, to the original field sample number.

#### **6.7.7.2.2 Re-Extractions/Re-Analyses**

When a sample is re-extracted and re-analyzed, the re-analysis data (as well as all associated supporting documentation) shall be reported in the data package.

The "field sample number" for the re-extraction/re-analysis results shall be the original field sample number with "RE" appended.

If multiple re-extractions and re-analyses are performed on the same sample, all analysis results and supporting documentation shall be reported. Re-extractions and re-analyses shall be distinguished by appending "RE1," "RE2," "RE3," and so on as necessary, to the original field sample number.

**Table 6-1 - Matrix Spike Recovery Limits**

<i>Parameter</i>	<i>Spike Added</i>	<i>Water Recovery Limits (%)</i>	<i>Solid Recovery Limits (%)</i>
<b>Organics</b>			
<b>Volatile Organics</b>			
full scan	1,1-dichloroethene	61-145	59-172
	trichloroethene	71-120	62-137
	chlorobenzene	75-130	60-133
	toluene	76-125	59-139
	benzene	76-127	66-142
Halogenated Volatile Organics	1,1-dichloroethene	61-145	59-172
	trichloroethene	71-120	62-137
	chlorobenzene	75-130	60-133
Non-Halogenated Volatiles	acetone	60 - 140	60 - 140
	isopropyl alcohol	60 - 140	60 - 140
	methyl ethyl ketone	60 - 140	60 - 140
Aromatic Volatile Organics	toluene	76-125	59-139
	benzene	76-127	66-142
Acrolein, Acrylonitrile, Acetonitrile	acrolein	60 - 140	60 - 140
	acrylonitrile	60 - 140	60 - 140
	acetonitrile	60 - 140	60 - 140
<b>Semivolatile Organics</b>			
Full scan	acenaphthene	46-118	31-137
	2,4-dinitrotoluene	24- 96	28- 89
	pyrene	26-127	35-142
	N-nitroso-di-n-propylamine	41-116	41-126
	pentachlorophenol	9-103	17-109
	phenol	12- 110	26- 90
	2-chlorophenol	27-123	25-102
	4-chloro-3-methylphenol	23- 97	26-103
	4-nitrophenol	10- 80	11-114
Phenols	pentachlorophenol	9-103	17-109
	Phenol	12- 110	26- 90
	2-chlorophenol	27-123	25-102
	4-chloro-3-methylphenol	23- 97	26-103
	4-nitrophenol	10- 80	11-114
Phthalate Esters	bis(2-ethylhexyl)phthalate	60 - 140	60 - 140
	butyl benzyl phthalate	60 - 140	60 - 140
	di-n-octyl phthalate	60 - 140	60 - 140
Nitroaromatics & Cyclic Ketones	2,4-dinitrotoluene	60 - 140	60 - 140
	1,4-dinitrobenzene	60 - 140	60 - 140
Chlorinated Hydrocarbons	2-chloronaphthalene	60 - 140	60 - 140
	1,4-dichlorobenzene	60 - 140	60 - 140
	hexachloropentadiene	60 - 140	60 - 140
Polynuclear Aromatic Hydrocarbons (PAH)	acenaphthene	46-118	31-137
	bezo(ghi)perylene	60 - 140	60 - 140
	fluoroanthene	60 - 140	60 - 140
	pyrene	26-127	35-142
Chlorinated Pesticides	gamma-BHC (lindane)	56-123	46-127
	heptachlor	40-131	35-130
	aldrin	40-120	34-132
	dieldrin	52-126	31-134
	endrin	56-121	42-139
	4,4'-DDT	38-127	23-134
PCBs	Aroclor 1221	50 - 150	50 - 150
	Aroclor 1248	50 - 150	50 - 150
Organophosphorous Pesticides	chlorpyrifos	50 - 150	50 - 150
	diazinon	50 - 150	50 - 150
	naled	50 - 150	50 - 150

**Table 6-1 - Matrix Spike Recovery Limits**

<i>Parameter</i>	<i>Spike Added</i>	<i>Water Recovery Limits (%)</i>	<i>Solid Recovery Limits (%)</i>
Chlorinated Herbicides	2,4-D	50 - 150	50 - 150
	dinoseb	50 - 150	50 - 150
Dioxins & Furans	1,2,3,4,7,8-HxCDD	50 - 150	50 - 150
	1,2,3,4,7,8-HxCDF	50 - 150	50 - 150
	1,2,3,4,5,6,7,8-OCDD	50 - 150	50 - 150
	1,2,3,4,5,6,7,8-OCDF	50 - 150	50 - 150
<b><i>Radiological Parameters</i></b>			
Radioactivity: Gross Alpha	NA	NA	NA
Gross Beta	NA	NA	NA
<b><i>Metals</i></b>			
Aluminum	Aluminum	75 - 125	75 - 125
Antimony	Antimony	75 - 125	75 - 125
Arsenic	Arsenic	75 - 125	75 - 125
Barium	Barium	75 - 125	75 - 125
Beryllium	Beryllium	75 - 125	75 - 125
Boron	Boron	75 - 125	75 - 125
Cadmium	Cadmium	75 - 125	75 - 125
Calcium	Calcium	75 - 125	75 - 125
Chromium	Chromium	75 - 125	75 - 125
Chromium VI	Chromium VI	75 - 125	75 - 125
Cobalt	Cobalt	75 - 125	75 - 125
Copper	Copper	75 - 125	75 - 125
Iron	Iron	75 - 125	75 - 125
Lead	Lead	75 - 125	75 - 125
Magnesium	Magnesium	75 - 125	75 - 125
Manganese	Manganese	75 - 125	75 - 125
Mercury	Mercury	75 - 125	75 - 125
Molybdenum	Molybdenum	75 - 125	75 - 125
Nickel	Nickel	75 - 125	75 - 125
Potassium	Potassium	75 - 125	75 - 125
Selenium	Selenium	75 - 125	75 - 125
Silica	Silica	75 - 125	75 - 125
Silver	Silver	75 - 125	75 - 125
Sodium	Sodium	75 - 125	75 - 125
Thallium	Thallium	75 - 125	75 - 125
Tin	Tin	75 - 125	75 - 125
Vanadium	Vanadium	75 - 125	75 - 125
Zinc	Zinc	75 - 125	75 - 125
<b><i>Wet Chemistry Parameters</i></b>			
Acidity (as calcium carbonate)	NA	NA	NA
Alkalinity (as calcium carbonate)	NA	NA	NA
Ammonia	Ammonia	80 - 120	80 - 120
Biochemical Oxygen Demand (BOD5)	See Note b	80 - 120	NA
Carbonaceous Biological Oxygen Demand (CBOD5)	See Note b	80 - 120	NA
Chemical Oxygen Demand (COD)	See Note b	80 - 120	NA
Chloride	Chloride	80 - 120	80 - 120
Chlorine total residual	Chlorine total residual	80 - 120	80 - 120
Coliform total	NA	NA	NA
Coliform,total	NA	NA	NA
Color	NA	NA	NA
Corrosivity	NA	NA	NA
Cyanide	Cyanide	80 - 120	80 - 120
Fluoride	Fluoride	80 - 120	80 - 120
Hardness	See Note g	80 - 120	NA

**Table 6-1 - Matrix Spike Recovery Limits**

<i>Parameter</i>	<i>Spike Added</i>	<i>Water Recovery Limits (%)</i>	<i>Solid Recovery Limits (%)</i>
Ignitability	NA	NA	NA
Moisture	NA	NA	NA
Nitrate	Nitrate	80 - 120	80 - 120
Nitrite	Nitrite	80 - 120	80 - 120
Total Kjeldahl Nitrogen (TKN)	Ammonia	80 - 120	NA
Oil & Grease	See Note a	80 - 120	
pH	NA	NA	NA
Phenols.total	Phenols.total	80 - 120	80 - 120
Phosphate, hydrolyzable	See Note f	80 - 120	NA
Phosphate, organic	See Note f	80 - 120	NA
Phosphate, ortho	See Note f	80 - 120	NA
Phosphorous, total	See Note f	80 - 120	80 - 120
Reactivity & Toxicity	NA	NA	NA
Residue, total (TS)	NA	NA	NA
Residue, filterable (TDS)	NA	NA	NA
Residue, non-filterable (TSS)	NA	NA	NA
Residue, settleable	NA	NA	NA
Residue, volatile (VS)	NA	NA	NA
Silica	Silica	80 - 120	80 - 120
Specific conductance	NA	NA	NA
Sulfate	Sulfate	80 - 120	80 - 120
Sulfide	Sulfide	80 - 120	80 - 120
Sulfite	Sulfite	80 - 120	80 - 120
Surfactants (MBAS)	See Note e	80 - 120	NA
Temperature	NA	NA	NA
Total organic carbon (TOC)	See Note c	80 - 120	80 - 120
Total organic halogens (TOX)	See Note d	80 - 120	NA
Total Petroleum Hydrocarbons	See Note a	80 - 120	80 - 120
Turbidity	NA	NA	NA

**Notes**

NA = Not Applicable

- a. spike with mixture of n-hexadecane, isooctane and chlorobenzene.
- b. spike with glucose-glutamic acid solution
- c. spike with potassium hydrogen phthalate.
- d. spike with trichlorophenol.
- e. spike with linear alkyl sulfonate.
- f. spike with  $\text{KH}_2\text{PO}_4$ .
- g. spike with  $\text{CaCO}_3$ .

**Table 6-2 - Matrix Spike Duplicate Precision Limits**

<i>Parameter</i>	<i>Spike Added</i>	<i>Maximum RPD for Waters</i>	<i>Maximum RPD for Soils</i>
<b>Organics</b>			
Volatile Organics			
full scan	1,1-dichloroethene	14	22
	trichloroethene	14	24
	chlorobenzene	13	21
	toluene	13	21
	benzene	11	21
Halogenated Volatile Organics	1,1-dichloroethene	14	22
	trichloroethene	14	24
	chlorobenzene	13	21
Non-Halogenated Volatiles	acetone	15	20
	isopropyl alcohol	15	20
	methyl ethyl ketone	15	20
Aromatic Volatile Organics	toluene	13	21
	benzene	11	21
Acrolein, Acrylonitrile, Acetonitrile	acrolein	15	20
	acrylonitrile	15	20
	acetonitrile	15	20
Semivolatile Organics			
Full scan	acenaphthene	31	19
	2,4-dinitrotoluene	38	47
	pyrene	31	36
	N-nitroso-di-n-propylamine	38	38
	pentachlorophenol	50	47
	phenol	42	35
	2-chlorophenol	40	50
	4-chloro-3-methylphenol	42	33
Phenols	4-nitrophenol	50	50
	pentachlorophenol	50	47
	phenol	42	35
	2-chlorophenol	40	50
	4-chloro-3-methylphenol	42	33
	4-nitrophenol	50	50
	bis(2-ethylhexyl)phthalate	40	50
	butyl benzyl phthalate	40	50
Phthalate Esters	di-n-octyl phthalate	40	50
	2,4-dinitrotoluene	40	50
	1,4-dinitrobenzene	40	50
Nitroaromatics & Cyclic Ketones	2-chloronaphthalene	40	50
	1,4-dichlorobenzene	40	50
	hexachloropentadiene	40	50
Chlorinated Hydrocarbons	acenaphthene	31	19
	bezo(ghi)perylene	40	50
	fluoroanthene	40	50
	pyrene	31	36
Polynuclear Aromatic Hydrocarbons (PAH)	gamma-BHC (lindane)	15	50
	heptachlor	20	31
	aldrin	22	43
	dieldrin	18	38
	endrin	21	45
	4,4'-DDT	27	50
Chlorinated Pesticides	Aroclor 1221	40	50
	Aroclor 1248	40	50
PCBs	chlorpyrifos	40	50
	diazinon	40	50
	naled	40	50
Organophosphorous Pesticides			

**Table 6-2 - Matrix Spike Duplicate Precision Limits**

<i>Parameter</i>	<i>Spike Added</i>	<i>Maximum RPD for Waters</i>	<i>Maximum RPD for Soils</i>
Chlorinated Herbicides	2,4-D	40	50
	dinoseb	40	50
Dioxins & Furans	1,2,3,4,7,8-HxCDD	40	50
	1,2,3,4,7,8-HxCDF	40	50
	1,2,3,4,5,6,7,8-OCDD	40	50
	1,2,3,4,5,6,7,8-OCDF	40	50

**Table 6-3 - Duplicate Sample Precision Limits**

<i>Parameter</i>	<i>Maximum RPD for Waters<sup>1</sup></i>	<i>Maximum RPD for Soils</i>
<b><i>Radiological Parameters</i></b>		
Gross Alpha	20	25
Gross Beta	20	25
<b><i>Metals</i></b>		
Aluminum	20	20
Antimony	20	20
Arsenic	20	20
Barium	20	20
Beryllium	20	20
Boron	20	20
Cadmium	20	20
Calcium	20	20
Chromium	20	20
Chromium VI	20	20
Cobalt	20	20
Copper	20	20
Iron	20	20
Lead	20	20
Magnesium	20	20
Manganese	20	20
Mercury	20	20
Molybdenum	20	20
Nickel	20	20
Potassium	20	20
Selenium	20	20
Silica	20	20
Silver	20	20
Sodium	20	20
Thallium	20	20
Tin	20	20
Vanadium	20	20
Zinc	20	20
<b><i>Wet Chemistry Parameters</i></b>		
Acidity (as calcium carbonate)	20	25
Alkalinity (as calcium carbonate)	20	25
Ammonia	20	25
Biochemical Oxygen Demand (BOD5)	20	25
Carbonaceous Biological Oxygen Demand (CBOD5)	20	25
Chemical Oxygen Demand (COD)	20	25
Chloride	20	25
Chlorine total residual	20	25
Coliform total	20	25

**Table 6-3 - Duplicate Sample Precision Limits**

<i>Parameter</i>	<i>Maximum RPD for Waters<sup>1</sup></i>	<i>Maximum RPD for Soils</i>
Coliform,total	20	25
Color	20	25
Corrosivity	20	25
Cyanide	20	25
Fluoride	20	25
Hardness	20	25
Ignitability	20	25
Moisture	20	25
Nitrate	20	25
Nitrite	20	25
Total Kjeldahl Nitrogen (TKN)	20	25
Oil & Grease	20	25
pH	20	25
Phenols,total	20	25
Phosphate, hydrolyzable	20	25
Phosphate, organic	20	25
Phosphate, ortho	20	25
Phosphorous, total	20	25
Reactivity & Toxicity	20	25
Residue, total (TS)	20	25
Residue, filterable (TDS)	20	25
Residue, non-filterable (TSS)	20	25
Residue, settleable	20	25
Residue, volatile (VS)	20	25
Silica	20	25
Specific conductance	20	25
Sulfate	20	25
Sulfide	20	25
Sulfite	20	25
Surfactants (MBAS)	20	25
Temperature	20	25
Total organic carbon (TOC)	20	25
Total organic halogens (TOX)	20	25
Total Petroleum Hydrocarbons	20	25
Turbidity	20	25

1. RPD limits apply if both sample and duplicate values are greater than or equal to 5x CRDL. If either sample or duplicate values are less than 5x CRDL, then the absolute difference between the two values must be less than the CRDL. If both values are below the CRDL, then precision specifications are not applicable.

**Table 6-4 - Surrogate Spiking Compounds**

Compounds	Fraction	Amount in Sample/Extract* (prior to dilution)	
		Water	Soil
Toluene-d8	VOA	50 ug	50 ug
4-Bromofluorobenzene	VOA	50 ug	50 ug
1,2-dichloroethane-d4	VOA	50 ug	50 ug
Nitrobenzene-d5	BNA	50 ug	50 ug
2-fluorobiphenyl	BNA	50 ug	50 ug
p-terphenyl-d14	BNA	50 ug	50 ug
1,2-Dichlorobenzene	BNA	50 ug	50 ug
Phenol-d5	BNA	75 ug	75 ug
2-Fluorophenol	BNA	75 ug	75 ug
2,4,6-Tribromophenol	BNA	75 ug	75 ug
2-Chlorophenol-d4	BNA	75 ug	75 ug
Tetrachloro-m-xylene	Pest	0.2 ug	0.2 ug
Decachlorobiphenyl	Pest	0.2 ug	0.2 ug

\* AT THE TIME OF INJECTION

**Table 6-5 - Acceptance Limits For Surrogate Recoveries**

Surrogate Compound	Fraction	Water	Soil	Soil (Methanol)
Toluene-d8	VOA	88-11*	84-138*	50-125*
4-Bromofluorobenzene	VOA	86-115	59-113	60-121*
1,2-Dichloroethane-d4	VOA	76-114	70-121	58-118
Nitrobenzene-d5	BNA	35-114*	23-120*	NA
2-Flourobiphenyl	BNA	43-116	30-115	NA
p-Terphenyl-d14	BNA	33-141	18-137	NA
1,2-dichlorobenzene-d4	BNA	16-110	20-130	NA
Phenol-d5	BNA	10-110	24-113	NA
2-Flourophanol	BNA	21-110	25-121	NA
2,4,6-Tribromophenol	BNA	10-123	19-122	NA
2-Chlorophenol-d4	BNA	33-110	20-130	NA
Tetrachloro-m-xylene	Pest	60-150*	60-150*	NA
Decachlorobiphenyl	Pest	60-150	60-150	NA

\* DNREC does not recognize advisory surrogate limits.

NA - Not Applicable

**Table 6-6 - BFB Criteria**

<b>m/e</b>	<b>ION ABUNDANCE CRITERIA</b>
50	8.0 - 40.0% of mass 95
75	30.0 - 66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0 - 9.0% of mass 95
173	Less than 2.0% of mass 174
174	50.0 - 120.0% of mass 95
175	4.0 - 9.0 % of mass 174
176	93.0 - 101.0% of mass 174
177	5.0 - 9.0% of mass 176

**Table 6-7 - DFTPP Criteria**

<b>m/e</b>	<b>ION ABUNDANCE CRITERIA (% RELATIVE ABUNDANCE)</b>
51	30.0- 80.0% of mass 198
68	Less than 2.0% of mass 69
69	Mass 69 relative abundance
70	Less than 2.0% of mass 69
127	25.0 - 75.0% of mass 198
197	Less than 1.0% of mass 198
198	Base Peak, 100% relative abundance
199	5.0 to 9.0% of mass 198
275	10.0- 30.0% of mass 198
365	Greater than 0.75% of mass 198
441	Present, but less than mass 443
442	40.0 - 110.0% of mass 198
443	15.0 - 24.0% of mass 442

Table 6-8 Minimum Practical Quantitation Limits

Compound	Practical Quantitation Limit (ug/Kg)
Aldrin	380
DDD	2000
DDE	1500
DDT	1500
Toxaphene	1000
Heptachlor	330
Endrin Ketone	2000
Dieldrin	400
Endrin	2000
Endosulfan I & II	2000
Endosulfan	2000
Sulfate	2000
Total PCB's*	830
Heptachlor Epoxide	330
Endrin Aldehyde	2000
Delta BHC	500
Alpha BHC	500
Beta BHC	500
Gamma BHC	500
Chlordane	1000
Methoxychlor	2000

\* Each specific Arochlor must have a practical quantitation limit below 830 ug/Kg.

**Table 6-9 - Internal Standard Specifications**

<i><b>Fraction</b></i>	<i><b>IS Compound</b></i>	<i><b>Concentration</b></i>
VOA	bromochloromethane	50 ug/L*
VOA	1,4-difluorobenzene	50 ug/L*
VOA	chlorobenzene-d5	50 ug/L*
BNA	1,4-dichlorobenzene-d4	20 ng/ul**
BNA	naphthalene-d8	20 ng/ul**
BNA	acenaphthene-d10	20 ng/ul**
BNA	phenanthrene-d10	20 ng/ul**
BNA	chrysene-d12	20 ng/ul**
BNA	perylene-d12	20 ng/ul**

\* in the sample at the time of purging

\*\* in the sample extract prior to injection

## ***7.0 SAMPLE ANALYSIS DELIVERABLES REQUIREMENTS***

The laboratory data package should contain sufficient information to demonstrate that the DNREC project's data quality objectives (DQOs) have been met. The end user of the data should be able to ascertain the precision, accuracy, representativeness, comparability, completeness and sensitivity (i.e., PARCCS indicators) of the data from the information present in the deliverable. The information necessary to demonstrate attainment of DQOs is a function of the level of analytical quality control applied to establish a minimum acceptable level of uncertainty for the intended data use by the end user. DNREC projects will be reported in one of four deliverable formats as defined by DQOs and the levels of analytical quality control they require.

### **7.1 Data Quality Objectives and Levels of Analytical Quality Control**

DQOs are established during the project planning phase and prior to the initiation of field sampling and analytical laboratory work. DQOs are to be included in the Project Quality Assurance Plan (PQAP) and they define the needed precision, accuracy, representativeness, comparability, completeness and sensitivity of the data. The DQO process must also establish the required level of data usability/defensibility and the associated level of documentation needed to satisfy the requirement.

The level of QC required at a site will be determined by the DNREC project manager, working in conjunction with the PRP representative, and documented in the PQAP. Table 7-1 outlines typical data uses as they relate to the four deliverables formats.

### **7.2 Data Deliverables Requirements**

#### **7.2.1 Level 1**

Level 1 deliverables are generally used with field or screening analyses. These produce qualitative or semiquantitative results, which are typically used for purposes such as delineation of contamination zones, characterization of contaminant functional group makeup (e.g., aromatic) and gross concentrations, or health and safety screening. Screening data is also sometimes used by laboratories to estimate concentration ranges prior to a more formal analysis. Screening data alone can not be used to eliminate concerns of suspected contamination at a site; confirmation is required regardless of whether screening analyses show positive or negative results. Generally, screening results are confirmed by sending a minimum of 10% of the samples to the laboratory for definitive analysis.

An extensive deliverable is generally not required. Typically, only sample results are reported, with little or no supporting documentation. Laboratories may report screening results from reports generated from the facility laboratory information management system (LIMS). LIMS reporting options typically include routines for reporting results only and results with QC summaries.

#### **7.2.1.1 Report Content**

The content of a Level 1 report is dependent upon the screening technique employed. A typical screening report should include the following information:

- Sample identification number
- Preparation method reference or brief summary
- Analysis method or brief summary
- Detection/reporting limits
- Identity and quantity (if applicable) of analyte(s) present
- Date and time of sample collection
- Date and time of sample analysis
- Field or screening instrument calibration

#### **7.2.1.2 QC Information**

Depending on the level of sophistication of screening methods employed, optional reporting may involve quality control samples (e.g., matrix spikes, sample duplicates, etc.), method blanks, and calibration standard results. Unless the PQAP specifies otherwise, Level 1 deliverables do not include any QC information.

### **7.2.2 Level 2**

Level 2 deliverables are generally used with routine, ongoing analytical programs where full documentation of QC measurements is not required as part of the report. Projects using Level 2 deliverables do not require validation of the analytical data, and the likelihood of results being used in litigation is very low. Ongoing groundwater monitoring programs are a good example of projects for which Level 2 deliverables might be requested. The PQAP may specify a Level 2 deliverable that includes partial or QC summary information.

A Level 2 deliverable includes a case narrative, sample results and, if specified in the PQAP, PARCCS (QC) information. Reports of sample results may be generated via the facility LIMS software.

#### **7.2.2.1 Report Content**

A case narrative should be included with each report. The case narrative should contain a table correlating client (or field) sample IDs and laboratory sample numbers, sample matrix, and information on the analytical methods performed. Deviations from requirements contained in the PQAP and laboratory SOPs should be discussed along with QC results that do not meet specifications and the corrective actions taken by the laboratory. Analytical result reports for each sample should contain the following information, at a minimum:

- Laboratory name and location
- Project name and sample delivery group (SDG) ID
- Client (or field) sample ID as written on COC form
- Laboratory sample ID number
- Matrix
- Sample preservation (this information may addressed in the case narrative)

- Date of sample collection
- Date of sample receipt by the laboratory
- Date sample extracted or prepared
- Date sample analyzed
- Method numbers (or reference) for all preparation, cleanup and analysis procedures
- Preparation and analysis batch numbers
- Analyte or parameter name
- Detection limits (DL) – estimated sample detection limits based on method detection limits (MDLs) adjusted for sample-specific factors (e.g., aliquot size, dilution or concentration factors, percent solids of soil or sediment)
- Practical quantitation or reporting limits
- Analytical results with the correct number of significant figures
- Any data qualifiers assigned
- Concentration units
- Dilution factor – all reported data shall reflect any dilutions and/or concentrations. The dilution factor, if applicable, should be noted on the analytical report.
- Percent solids (all soils, sediments, sludges, etc. are to be reported on a dry weight basis)

#### 7.2.2.2 QC Information

If requested by DNREC, the Level 2 data package must include summaries of specified laboratory QC data with their associated acceptance criteria. The deliverable should correlate the QC data (e.g., method blanks, LCS) with the associated samples and should clearly identify batch numbers. Method and matrix QC data must include all spike nominal concentrations, the spiked sample concentration results and calculated recoveries; all measures of precision, including relative percent difference (RPD); and all specified limits for accuracy and precision. This includes laboratory performance information such as results for method blanks, recoveries for LCSs, RPDS for LCS/LCSD sets, and recoveries for QC sample surrogates; and matrix-specific information such as matrix sample duplicate RPDs, MS and MSD recoveries, MS/MSD RPDs, field sample surrogate recoveries, serial dilutions, and post-digestion spikes, etc. Any sample results affected by QC results that do not meet specifications should be qualified (flagged) and discussed in the case narrative.

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***NOTE: The level of deliverable requested is independent of the analytical QC required for a project. If a level 2 deliverable with no QC summaries is requested, but project specifications include a full suite of QC measurements (MS/MSD, surrogates, blanks, spiked blanks, etc.), the laboratory must run all specified QC and the information must be readily retrievable by the laboratory at DNREC's request.***

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#### 7.2.3 Level 3 and Level 4

Level 3 and 4 deliverables are intended to document all steps taken by the laboratory to generate the reported results. As such, the package must be complete, clear, and accurate and should contain sufficient supporting documentation to allow the results to be reviewed and/or the data validated by an independent party without any further communication with the laboratory. The data package, therefore, must be able to stand alone in representing exactly what was done to a sample in order to generate the values that were reported (and, most likely, used to make

decisions) including referencing specific analytical methods and any modifications to those methods (e.g., performance-based protocol).

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***NOTE: The content and order of information specified for Level 3 and 4 deliverables is similar to the US Environmental Protection Agency's Contract Laboratory Program Statement(s) of Work. However, DNREC requirements are not exactly the same and must be reviewed carefully to ensure full reporting compliance. In addition, the PQAP may specify different requirements to better meet project needs.***

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Data packages should reflect the entire history of the samples from the time they were collected to the time final results were reported. This becomes especially important when, as is sometimes the case, analytical data is critically reviewed months or years after generation. Often, by the time data are reviewed, analytical methods have changed; procedures have been modified; personnel at the laboratory at the time of the analyses are no longer employed there; and memories have failed. Filling information gaps at this later date may not be possible. Consequently, data packages must be complete at the time they are generated.

A Level 3 deliverable contains summary forms that provide complete documentation of all steps taken by the laboratory. A Level 3 deliverable permits verification of the validity of the reported results. A Level 4 deliverable contains all of the summary forms in a Level 3 deliverable, and also includes raw data documenting the information in the summary forms. As the most complete deliverable format, a Level 4 report permits complete reproduction of all reported results and full validation of all data by an independent third party.

#### **7.2.4 Content**

Data packages may be presented based on a Sample Delivery Group (SDG) or on an analytical batch. While SDG's are convenient for grouping samples, they are administrative in nature and lack any technical rationale for the grouping. The SDG format fosters inclusion, in a single data package, of multiple analytical batches for some parameters and partial analytical batches for other parameters. The assembly and technical review of a data package presented in this manner can be complicated and confusing. Consequently, unless otherwise specified and agreed to by DNREC, data will be reported on an analytical batch basis.

When reported based on an analytical batch, all project samples analyzed in a single batch must be reported in a single data package. As a consequence, each data package will contain only one analytical fraction (e.g., volatiles, semivolatiles, metals, etc.). Samples within an analytical batch belonging to administrative groups such as SDG's, one or more chains of custody, site locations, etc., shall not be segregated and reported as separate data packages.

When based on a Sample Delivery Group (which must be specifically approved by DNREC), the data package shall contain all of the analytical results for all of the samples in the SDG. This may include samples in more than one analytical batch and more than one analytical parameter. When more than one analytical batch is reported, all of the quality control results including instrument tuning, calibration results, QC sample results, etc., for each of the analytical batches must be included in the data package to properly support the data. Each of the parameters must be presented in the order shown in Table 7-2. Information for each parameter will include and be arranged in the sequence indicated in Table 7-2.

### 7.2.5 Format

All pages must be sequentially numbered in the bottom right-hand corner, beginning with the first page of the Narrative.

If, after numbering all of the pages in a data package but before delivery to DNREC, a review of the package shows that some pages were inadvertently omitted, the new pages may be inserted into the proper locations and labeled alphabetically using the number on the preceding page as a precursor. For example, if three pages need to be inserted after page 13, they will be labeled as 13A, 13B, and 13C.

If, as a result of DNREC (or their authorized representative) review, pages are found to be missing or in error, the new pages will be numbered as described above, with an "R" following the page number. For example, if pages 13 & 14 required revision as a result of DNREC review, the replacement pages would be numbered 13R and 14R. If pages that were added by the laboratory prior to delivery to DNREC, numbered as described above (13A and 13B), required revision as a result of DNREC review, the replacement pages would be numbered 13AR and 13BR.

All copies must be legible. Reduction to approximately 95% of the original size is strongly recommended for all copies to avoid loss of information near the edges of each page. Ensuring that all pages are legible and clearly display all information recorded on the original page is the responsibility of the laboratory.

A sheet of colored paper must be placed after the last page of every major section (e.g., Narrative, Parameter, Field Records, etc.) and, if multiple parameters are reported, after the last page of each parameter. This applies to all copies of the data package as well as to the original.

### 7.2.6 Sequence of Presentation

The parameter sections of the data package shall be arranged as listed in Table 7-2. The information required within an individual parameter section shall be organized as indicated.

#### 7.2.6.1 *Parameter Data Order*

For data packages reporting data in the SDG format, parameter order shall be as follows:

- 1) GC/MS volatiles
- 2) GC/MS semivolatiles
- 3) Pesticide/PCB's
- 4) Other GC methods
- 5) Metals (by analysis technique)
  - a) Inductively coupled plasma spectroscopy
  - b) Atomic absorption spectroscopy
  - c) Cold vapor atomic absorption spectroscopy (for mercury)
- 6) Anions (alphabetically)
- 7) Miscellaneous parameters (alphabetically)

## **7.2.7 Sectional Content Requirements and Forms Instructions**

### **7.2.7.1 *Narrative***

The Narrative section of the data package must contain, at a minimum, the following information:

#### **7.2.7.1.1 List of Samples**

A table correlating field sample numbers and laboratory sample numbers. The table shall also indicate the date collected, date received, and parameters reported for all samples listed.

#### **7.2.7.1.2 Method References**

Specific analytical method references for all parameters being reported shall be listed. The references shall include separate sample preparation citations if the preparation procedures used were not part of the analytical method. If modifications to the written procedure or if performance-based protocols were used, the relevant information will be described. When a written analytical method allows a choice of procedure, the selected option shall be identified in this section. If the analytical method is not available in the open literature, a copy of the complete method shall be included in the data package.

#### **7.2.7.1.3 Special Instructions**

Any special instructions received, other than those documented on the field records, phone logs, client correspondence, etc., shall be noted in the data package. Special instructions may clarify specific guidance regarding the handling or processing of samples.

#### **7.2.7.1.4 Table of pH Values**

As a precaution against loss of contaminants, the handling and manipulation of samples for volatile organic compounds prior to analyses is minimized. Consequently, the pH of a sample analyzed for volatile organic compounds cannot be taken until after the sample has been analyzed. For all water samples analyzed for volatile organic compounds, a table of the pH values measured after analyses shall be included in the data package.

#### **7.2.7.1.5 Summary of Dilutions**

Analytical methods generally specify the quantity of the sample aliquot to be taken for analysis as well as the final volume of the extract or digestate after processing. Equations for calculating concentrations in the original sample from measurements of the concentrations in the extract are, consequently, defined and routine. Occasionally, however, the final extract needs to be diluted beyond the routine procedure due to high concentrations of materials or other problems. In calculating the concentration in the original sample, the dilution factor must be applied to obtain the correct concentration. The need for dilution of samples may also suggest some thoughts to the data user regarding the general nature of the samples. Consequently, a summary of the dilutions performed on the samples and the dilution factors used for each sample will be included in the narrative section.

#### **7.2.7.1.6 Discussion of QC Results**

In an attempt to ensure reliable results, various aspects of the analytical process are monitored through quality control checks. The results of this QC monitoring shall be summarized for those instances in which specified criteria were not met. The actions taken in each case and the results of the action must be discussed. Required corrective actions must be identified with appropriate supporting data included as an attachment.

The summary should address any and all deviations from acceptable analytical performance including internal standards, surrogate recoveries, calibration problems, QC samples, etc., for each fraction reported. All detected analytes in any blank (instrument, method, field, etc.) must be listed along with the unique blank ID, date extracted, and date analyzed. Attributing a deviation to a particular cause must include the rationale for deciding on the cause. Simply dismissing poor matrix spike recovery as a “matrix effect” without supporting evidence or logic, for example, would not be considered a satisfactory investigation of the problem.

#### 7.2.7.1.7 Discussion of Analytical Problems

A discussion of any and all problems encountered during the course of sample analyses such as missed holding times, chain of custody discrepancies, system malfunctions, etc., that may have had an adverse effect on the sample results must be included. The actions taken to resolve the problem will be discussed as well as the potential impact on the reported results.

#### 7.2.7.2 *Gas Chromatography/Mass Spectroscopy (GC/MS)*

Data generated by analysis by GC/MS shall be organized and submitted in the order given below. If GC/MS methods are used for more than one parameter, then this section shall be repeated in its entirety for each parameter.

##### 7.2.7.2.1 Quality Control (QC) Summary

The following summary forms shall be provided, in the indicated order:

- 1) Surrogate Recovery (CLP Form 2 or equivalent)
- 2) MS/MSD Recovery (CLP Form 3 or equivalent)
- 3) Instrument Blank Summary (CLP Form 4 or equivalent)
- 4) Method Blank Summary (CLP Form 4 or equivalent)
- 5) GC/MS Instrument Performance Check (CLP Form 5 or equivalent)
- 6) Internal Standard Area and RT Summary (CLP Form 8 or equivalent)

When more than one of any summary form is required, the multiple forms shall be organized chronologically, by instrument. For example, all method blank summaries on Instrument A would be presented in chronological order, followed by all method blank summaries on Instrument B in chronological order, etc.

##### 7.2.7.2.2 Sample Data

Sample data shall be presented in order of increasing field sample numbers, taking into account both alphabetic and numeric characters. If more than one analysis is reported for a sample, the original analysis shall be presented first, followed immediately by any re-analyses. For each sample analysis, the following documentation shall be provided, in the indicated order:

- 1) Organic Analysis Data Sheet-TCL's (CLP Form 1 or equivalent)

- 2) Organic Analysis Data Sheet-TIC's (CLP Form 1 or equivalent)
- 3) **(Level 4 only)** Reconstructed Ion Chromatogram (RIC), to include:
  - a) Normalized on the largest nonsolvent peak;
  - b) Accurately labeled with all internal standard and surrogate peaks ("IS" and "S" above the peak will suffice if the QR includes the peak RT and the full compound name); and
  - c) Labeled with header information to include field (laboratory) sample number, date and time of analysis, instrument ID, and laboratory filename.
- 4) **(Level 4 only)** Quantitation Report (QR), to include:
  - a) Retention time and scan number of target compounds;
  - b) Ion used to quantitate each compound;
  - c) Qualifier flags on manually integrated areas;
  - d) Hardcopy of all manual integrations showing the enhanced peak (ion) integrated and resulting area; this area must match the flagged area on the QR;
  - e) Header information same as for RIC; and
  - f) Entries for apparent hits that are determined to be false positives from evaluation of the mass spectra shall be labeled as "false positive" on the QR.
- 5) **(Level 4 only)** Mass Spectra, in order as found on QR, to include:
  - a) Raw and background-subtracted from sample;
  - b) For all apparent hits on the QR (i.e., for all compounds with apparent concentration above the detection limit);
  - c) Background-subtracted standard spectrum for each apparent target compound hit;
  - d) Labeled with field sample number, lab file ID, date and time of analysis, instrument ID, and compound name; and
  - e) Sample spectra that do not confirm the identification on the QR shall be labeled as "False Positive" or "false +."
- 6) **(Level 4 only)** NIST Library Searches, to include:
  - a) For all eligible extraneous peaks, in retention time order;
  - b) "Eligible" peaks will include target compound false positives of sufficient peak height that are not otherwise accounted for;
  - c) Labeled with field sample number, lab file ID, date and time of analysis, and instrument ID;
  - d) Conclusion of analyst with respect to peak identification to be reported shall be clearly noted, initialed, and dated. For example:
    - i) If an extraneous peak in the semivolatile fraction is identified as a volatile target compound, the search page shall be noted as "volatile TCL - not reported", with initials and a date.
    - ii) If none of the searches generate a good match with the sample spectrum, the search page shall be noted as "unknown", with initials and date.
    - iii) If any of the searches is determined to be an acceptable identification, then that entry on the search page shall be flagged (circled, checked, asterisked, etc.), and initialed and dated.

#### 7.2.7.2.3 Standards Data

All standards supporting the analysis of the samples in the data package must be provided. This includes initial and continuing calibration standards for all original and repeat sample analyses. For a single calibration series on a single instrument, the following documentation must be included, in the order indicated.

##### 7.2.7.2.3.1 Initial Calibration Standards (ICS)

For the initial calibration standard (ICS), the following information must be provided in the data package:

- 1) GC/MS Initial Calibration Data (CLP Form 6 or equivalent)
- 2) **(Level 4 only)** RIC and Quantitation Report (QR), to include:
  - a) Each ICS standard must be organized in order of lowest to highest concentration;
  - b) QR must show quantitation ion used for each target analyte;
  - c) All manually integrated areas must be identified with “M” flags on QR and include a hardcopy of each manual integration, showing the peak (ion) integrated and the resulting area (this area must match the flagged area on the QR);
  - d) Header information on RIC and Q must include standard concentration, standard solution ID number(s), date and time of analysis, lab file ID, and instrument ID.

#### 7.2.7.2.3.2 Continuing Calibrations Standards (CCS)

Each shift standard associated with the ICS (i.e., on the same instrument until another ICS was analyzed) and applicable to the reported samples shall be documented as follows:

- 1) GC/MS Continuing Calibration Data (CLP Form 7 or equivalent)
- 2) (Level 4 only) RIC and Quantitation Report (QR), to include:
  - a) QR must show quantitation ion used for each target analyte;
  - b) All manually integrated areas must be identified with “M” flags on QR and include a hardcopy of each manual integration showing the peak (ion) integrated and the resulting area (this area must match the flagged area on the QR); and
  - c) Header information as for ICS, above.

Multiple continuing calibration standards shall be placed in chronological order by instrument, immediately after the ICS in the data package.

#### 7.2.7.2.3.3 Multiple Initial Calibrations

Initial calibration sections for each analytical parameter category in this document define the documentation required for a single initial calibration standard on a given instrument along with the applicable continuing calibration standards associated with that ICS. In cases when more than one ICS must be reported, the following order will be required:

- 1) Multiple ICS/CCS data for a particular instrument will be provided in chronological order.
- 2) ICS/CCS data for a second instrument will be provided after all the standards for the first instrument.

The goal is to present the standards in the order in which they were analyzed, making their review and evaluation as straightforward as possible.

If all of the samples are analyzed in a single analytical batch, as intended, then the number of different calibration standards (ICS and CCS) to be reported in any given data package will be minimized. If some samples in an analytical batch must be re-analyzed (re-extracted and re-injected), the new analytical batch must be reported in a different data package if reporting is done on an analytical batch basis. If reporting is done on a SDG basis or if re-analysis involves only re-injection, the later data will be included in the data package with the initial data.

#### 7.2.7.2.4 Raw Quality Control (QC) Data

Section 7.2.7.2.1 outlines the forms that must be included in the data package to summarize the QC results. The following sections describe the documentation required to support results reported on the summary forms.

#### 7.2.7.2.4.1 *Tuning Compound Runs (Level 4 only)*

For each BFB or DFTPP tuning analysis performed, the following data must be included in the data package (**Level 4 only**):

- 1) Mass Spectrum, clearly indicating the background subtraction used to generate it;
- 2) Mass Listing, also indicating the background subtraction used; and
- 3) Reconstructed Ion Chromatogram.

Header information on each of the 3 raw data items listed above must include instrument ID, standard solution ID number, date and time analyzed, and lab filename.

Documentation of a BFB/DFTPP run is required for every analysis shift applicable to the samples reported in the data package; this includes the shift(s) on which each initial calibration was performed.

Raw data for multiple analyses of BFB/DFTPP shall be in chronological order for each instrument with all data provided for one instrument followed by, if applicable, all data for the next instrument and so on.

#### 7.2.7.2.4.2 *Instrument Blanks (IB)*

For each IB analyzed in association with the reported samples, the following information must be included in the data package:

- 1) Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent)
- 2) Organic Analysis Data Sheet - TIC's (CLP Form 1 or equivalent)
- 3) (**Level 4 only**) RIC, QR, Mass Spectra, and Library Searches
  - a) In the same order as for samples
  - b) In the same format as for samples
  - c) With the same notations as for samples
  - d) Note that library searches are required on all visible extraneous peaks in IB's

Multiple IB's shall be in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

#### 7.2.7.2.4.3 *Method Blanks (MB)*

For each MB analyzed in association with the reported samples, the following information must be included in the data package:

- 1) Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent)
- 2) Organic Analysis Data Sheet - TIC's (CLP Form 1 or equivalent)
- 3) (**Level 4 only**) RIC, QR, Mass Spectra, and Library Searches
  - a) In the same order as for samples;
  - b) In the same format as for samples;
  - c) With the same notations as for samples;
  - d) Note that library searches are required on all visible extraneous peaks in MB's.

Multiple MB's (or multiple analyses of a single MB) shall be presented in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

#### 7.2.7.2.4.4 *Matrix Spike/Matrix Spike Duplicates (MS/MSD)*

For each MS/MSD pair analyzed in association with the reported samples, the following information must be included in the data package:

- 1) Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent)
  - a) Results for all spike and non-spike compound hits shall be reported as the numerical concentration value calculated from the raw data;
  - b) The "EPA Sample Number" (or field sample number) recorded in the top right corner shall be comprised of the field sample number of the original sample used for the QC analyses, with a suffix of "MS" or "MSD." Note: The EPA or field sample number is the sample identifier found on the field chain of custody and not the number assigned by the laboratory.
  - c) (Level 4 only) RIC and QR - in the same format and with the same notations as described in Section 7.3.5.2.2 for samples.

#### 7.2.7.2.5 Screening Data

If samples were screened (i.e., analyzed separately from and prior to the reported analysis data in order to determine the appropriate dilution factor), then the following information shall be provided at this point in the data package:

1. Screening results report (e.g., LIMS generated report)
2. **(Level 4 only)** Raw data printout (chromatograms, strip charts, integrator output, etc.) showing field sample number, instrument ID, date/time of analysis, lab filename, and analysis conditions;
3. Manual calculation of "X Factor", with analyst initials and date;
4. **(Level 4 only)** Raw data printout(s) for associated standard and blank analyses showing standard composition and concentration, instrument ID, date/time of analysis, and lab filename.

#### 7.2.7.2.6 Supporting Laboratory Records

Copies of the following laboratory documents must be provided in the data package:

- 1) Extraction Logs clearly identifying all reported samples (original and repeat preparations, where applicable);
- 2) Instrument Run Logs clearly identifying all reported samples (original and repeat analyses, where applicable);
- 3) Standard Preparation Logs including all working, secondary, and stock solutions used to support the reported analyses;
- 4) Internal chain of custody records, documenting the flow of each sample through the various laboratory departments during preparation, storage, and analysis;
- 5) Weigh logs (soil samples) indicating tare and final weights when taking the aliquot for analysis;
- 6) Percent moisture log (for solid samples) indicating tare, initial (tare plus solid aliquot), and final (tare plus solid aliquot after heating) weights;

- 7) Screening log clearly identifying all reported samples (original and repeat analyses, where applicable);
- 8) Cleanup log identifying all reported samples (where applicable) subjected to cleanup procedures.

#### 7.2.7.3 *Gas Chromatography (GC)*

Data generated by GC analyses shall be organized and submitted according to the schedule discussed below. If GC methods are used for more than one parameter, then this section shall be repeated in its entirety for each parameter.

##### 7.2.7.3.1 Quality Control (QC) Summary

The following summary forms shall be provided, in the indicated order:

1. Surrogate Recovery (CLP Form 2 or equivalent)
2. MS/MSD Recovery (CLP Form 3 or equivalent)
3. Instrument Blank Summary (CLP Form 4 or equivalent)
4. Method Blank Summary (CLP Form 4 or equivalent)

When more than one of any summary form is required, the multiple forms shall be organized chronologically, by instrument. For example, all method blank summaries on Instrument A would be presented in chronological order, followed by all method blank summaries on Instrument B in chronological order, etc.

##### 7.2.7.3.2 Sample Data

Sample data shall be presented in order of increasing field sample numbers, taking into account both alphabetic and numeric characters. If more than one analysis is reported for a sample, the original analysis shall be presented first, followed immediately by any re-analyses. For each sample analysis, an Organic Analysis Data Sheet (CLP Form 1 or equivalent) will be submitted. Additionally, **for Level 4 data packages only**, the following will be submitted:

- 1) Gas Chromatogram, to include:
  - a) Normalized on the largest nonsolvent peak;
  - b) Accurately labeled with all internal standard (if applicable) and surrogate peaks (“IS” and “S” above the peak will suffice if the QR includes the peak RT and the full compound name); and
  - c) Labeled with header information to include field (laboratory) sample number, date and time of analysis, instrument ID, and laboratory filename.
- 2) Quantitation Report (QR), to include:
  - a) Retention time of target compounds;
  - b) “M” flags on manually integrated areas;
  - c) Hardcopy of all manual integrations showing the peak integrated and resulting area; this area must match the flagged area on the QR.

##### 7.2.7.3.3 Standards Data

All standards supporting the analysis of the samples in the data package must be provided. This includes initial and continuing calibration standards for all original and repeat sample analyses. For a single calibration series on a single instrument, the following documentation must be included, in the order indicated.

#### 7.2.7.3.3.1 *Initial Calibration Standards (ICS) and Evaluation Mixtures*

For the initial calibration standard (ICS), the following information must be provided in the data package:

- 1) GC Initial Calibration Data (CLP Form VI PEST-1, -2, -3 or equivalent)
- 2) **(Level 4 only)** Gas chromatogram and Quantitation Report (QR), to include:
  - a) Each ICS standard must be organized in order of lowest to highest concentration;
  - b) QR must show the retention time used for each target analyte;
  - c) All manually integrated areas must be identified with “M” flags on QR and include a hardcopy of each manual integration, showing the peak integrated and the resulting area (this area must match the flagged area on the QR);
  - d) Header information on QR must include standard concentration, standard solution ID number(s), date and time of analysis, lab file ID, and instrument ID.
- 3) Analyte resolution summary (CLP Form VI PEST-4 or equivalent)
  - a) **(Level 4 only)** chromatogram and QR, as discussed above
- 4) Performance evaluation mixture (CLP Form VI PEST-5 or equivalent)
  - a) **(Level 4 only)** chromatogram and QR, as discussed above
- 5) Individual standard mixture A (CLP Form VI PEST-6 or equivalent)
  - a) **(Level 4 only)** chromatogram and QR, as discussed above
- 6) Individual standard mixture B (CLP Form VI PEST-7 or equivalent)
  - a) **(Level 4 only)** chromatogram and QR, as discussed above

#### 7.2.7.3.3.2 *Continuing Calibration Standards (CCS)*

Each shift standard associated with the ICS (i.e., on the same instrument until another ICS was analyzed) and applicable to the reported samples shall be documented as follows:

- 1) GC Continuing Calibration Data (CLP Form VII PEST-1, -2 or equivalent)
- 2) **(Level 4 only)** Gas Chromatogram and Quantitation Report (QR), to include:
  - a) QR must show retention time used for each target analyte;
  - b) All manually integrated areas must be identified with “M” flags on the QR and include a hardcopy of each manual integration showing the peak integrated and the resulting area (this area must match the flagged area on the QR);
  - c) Header information as for ICS, above.

Multiple continuing calibration standards shall be placed in chronological order immediately after the ICS in the data package.

#### 7.2.7.3.3.3 *Multiple Initial Calibrations*

Initial calibration sections for each analytical parameter category in this document define the documentation required for a single initial calibration standard on a given instrument along with the applicable continuing calibration standards associated with that ICS. In cases when more than one ICS must be reported, the following order will be required:

1. Multiple ICS/CCS data for a particular instrument will be provided in chronological order.

2. ICS/CCS data for a second instrument will be provided after all the standards for the first instrument.

The goal is to present the standards in the order in which they were analyzed, making their review and evaluation as straightforward as possible.

If all of the samples are analyzed in a single analytical batch, as intended, then the number of different calibration standards (ICS and CCS) to be reported in any given data package will be minimized. If some samples in an analytical batch must be re-analyzed (re-extracted and re-injected), the new analytical batch must be reported in a different data package if reporting is done on an analytical batch basis. If reporting is done on a SDG basis or if re-analysis involves only re-injection, the later data will be included in the data package with the initial data.

#### 7.2.7.3.3.4 *Additional GC Standards Forms*

When applicable, the following additional GC standards forms (**and associated raw data for Level 4 data packages**) will be included in the standards section of the data package, in the listed order:

1. Analytical sequence and surrogate standard retention time summary (CLP Form VIII PEST or equivalent)
2. Florisil cartridge check (CLP Form IX PEST-1 or equivalent)
3. Pesticide GPC calibration (CLP Form IX PEST-2 or equivalent)
4. Pesticide identification summary for single component analytes (CLP Form X PEST-1 or equivalent)
5. Pesticide identification summary for multicomponent analytes (CLP Form X PEST-2 or equivalent)

#### 7.2.7.3.4 Raw Quality Control (QC) Data

Section 7.2.7.3.1 outlines the forms that must be included in the data package to summarize the GC QC results. The following sections describe the documentation required as supporting evidence for the results reported on the summary forms.

##### 7.2.7.3.4.1 *Instrument Blanks (IB)*

For each IB analyzed in association with the reported samples, an Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent) must be included in the data package. **Level 4 data packages** also require copies of the associated chromatogram and QR raw data in the same format and with the same notations as described in Section 7.2.7.3.2 for samples to follow the IB result form.

Multiple IB's shall be in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

##### 7.2.7.3.4.2 *Method Blanks (MB)*

For each MB analyzed in association with the reported samples, an Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent) must be included in the data package. **Level 4 data packages** also require copies of the associated chromatogram and QR raw data in the same format and with the same notations as described in Section 7.2.7.3.2 for samples to follow the MB result form.

Multiple MB's (or multiple analyses of a single MB) shall be presented in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

#### 7.2.7.3.4.3 *Matrix Spike/Matrix Spike Duplicates (MS/MSD)*

For each MS/MSD pair analyzed in association with the reported samples, the following information must be included in the data package:

- 1) Organic Analysis Data Sheet - TCL's (CLP Form 1 or equivalent)
  - a) Results for all spike and non-spike compound hits shall be reported as the numerical concentration value calculated from the raw data.
  - b) The field sample number recorded in the top right corner shall be comprised of the field sample number of the original sample used for the QC analyses, with a suffix of "MS" or "MSD". Note: The field sample number is the sample identifier found on the field chain of custody and not the number assigned by the laboratory.
- 2) **(Level 4 only)** Chromatogram and QR - in the same format and with the same notations as described in Section 7.2.7.3.2 for samples.

#### 7.2.7.3.5 Screening Data

If samples were screened (i.e., analyzed separately from and prior to the reported analysis data in order to determine the appropriate dilution factor), then the following information shall be provided at this point in the data package:

1. Screening results report (e.g., LIMS generated report)
2. **(Level 4 only)** Raw data printout (chromatograms, strip charts, integrator output, etc.) showing field sample number, instrument ID, date/time of analysis, lab filename, and analysis conditions;
3. Manual calculation of "X Factor", with analyst initials and date;
4. **(Level 4 only)** Raw data printout(s) for associated standard and blank analyses showing standard composition and concentration, instrument ID, date/time of analysis, and lab filename.

#### 7.2.7.3.6 Supporting Laboratory Records

Copies of the following laboratory documents must be provided in the data package:

1. Extraction Logs clearly identifying all reported samples (original and repeat preparations, where applicable);
2. Instrument Run Logs clearly identifying all reported samples (original and repeat analyses, where applicable);
3. Standard Preparation Logs including all working, secondary, and stock solutions used to support the reported analyses;
4. Internal chain of custody records, documenting the flow of each sample through the various laboratory departments during preparation, storage, and analysis;
5. Weigh logs (soil samples) indicating tare and final weights when taking the aliquot for analysis;
6. Percent moisture log (for solid samples) indicating tare, initial (tare plus solid aliquot), and final (tare plus solid aliquot after heating) weights;

7. Screening log clearly identifying all reported samples (original and repeat analyses, where applicable);
8. Cleanup log identifying all reported samples (where applicable) subjected to cleanup procedures.

#### **7.2.7.4 Metals**

##### **7.2.7.4.1 Quality Control (QC) Summary**

The following summary forms shall be provided, in the indicated order:

1. Analysis Data Sheet-TCL (CLP Form 1 or equivalent)
2. Initial Calibration Data (CLP Form 2A or equivalent)
3. Continuing Calibration Data (CLP Form 2A or equivalent)
4. Low Level Standard Data (CLP Form 2B or equivalent)
5. Calibration and Preparation Blank Data (CLP Form 3A & B or equivalent)
6. Interference Check Sample Data (CLP Form 4 or equivalent) (ICP only)
7. Matrix Spike Recovery Data (CLP Form 5 or equivalent)
8. Duplicate Precision (CLP Form 6 or equivalent)
9. Laboratory Control Sample Data (CLP Form 7 or equivalent)
10. Standard Additions Data (CLP Form 8 or equivalent) (if applicable)
11. ICP Serial Dilution Data (CLP Form 9 or equivalent)
12. Instrument Detection Limits (CLP Form 10 or equivalent)
13. ICP Linear Range Data (CLP Form 12 or equivalent)
14. Preparation Log (CLP Form 13 or equivalent)
15. Analysis Run Log (CLP Form 14 or equivalent) including entries for post-digest spike recoveries for furnace metals

When more than one of any summary form is required, the multiple forms shall be organized chronologically, by instrument. For example, all method blank summaries on Instrument A would be presented in chronological order, followed by all method blank summaries on Instrument B in chronological order, etc. Additionally, ICP data will be presented before AA data.

##### **7.2.7.4.2 Sample Data**

Sample data shall be presented in order of increasing field sample numbers, taking into account both alphabetic and numeric characters. If more than one analysis is reported for a sample, the original analysis shall be presented first, followed immediately by any re-analyses. For each sample, an Inorganic Analysis Data Sheet (CLP Form 1 or equivalent) will be submitted. Additionally, **for Level 4 data packages**, the instrument quantitation report (QR), containing the following information, will be included in the Instrument Raw Data section:

1. Sample ID
2. Date and time of analysis
3. Instrument ID
4. Names of target elements (preferred in alphabetical order)
5. Instrument replicate response readings for each element
6. Dilution factor
7. Calculated concentration

#### 7.2.7.4.3 Standards Data

All standards supporting the analysis of the samples in the data package must be provided **for Level 4 deliverables**. This includes initial calibration, initial verification, and continuing verification calibration standards for all original and repeat sample analyses. For a single calibration series on a single instrument, the following documentation must be included, in the order indicated.

##### 7.2.7.4.3.1 Initial Calibration Standards

For the initial calibration standard sequence, the following quantitation reports must be provided **in the Level 4 data package**:

1. Initial Blank
2. Initial Calibration Standard with concentration clearly identified
3. Initial Calibration Verification Standards with sources and concentrations clearly identified

##### 7.2.7.4.3.2 Continuing Calibration Verification Standards

Quantitation reports for continuing calibration verification standards will be submitted with sources and concentrations clearly identified **(Level 4 only)**.

##### 7.2.7.4.3.3 Multiple Initial Calibrations

Sections 7.2.7.4.3.1 and 7.2.7.4.3.2 define the documentation required for a single initial calibration on a given instrument along with the applicable continuing calibration verification standards associated with that calibration. In cases when more than one calibration set must be reported, the following order will be required:

1. Multiple calibration data for a particular instrument will be provided in chronological order.
2. Calibration data for a second instrument will be provided after all the standards for the first instrument.

The goal is to present the standards in the order in which they were analyzed, making their review and evaluation as straightforward as possible.

If all of the samples are analyzed in a single analytical batch, as intended, then the number of different calibration standards to be reported in any given data package will be minimized. If some samples in an analytical batch must be re-analyzed (re-digested and re-injected), the new analytical batch must be reported in a different data package if reporting is done on an analytical batch basis. If reporting is done on a SDG basis or if re-analysis involves only re-injection, the later data will be included in the data package with the initial data.

#### 7.2.7.4.4 Raw Quality Control (QC) Data

Section 7.2.7.4.1 outlines the forms that must be included in the data package to summarize the QC results. The following sections describe the documentation required as supporting evidence for the results reported on the summary forms.

#### 7.2.7.4.4.1 *Instrument Blanks (IB)*

For each IB analyzed in association with the reported samples, an Inorganic Analysis Data Sheet (CLP Form 1 or equivalent) must be included in the data package.

Multiple IB's shall be in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

#### 7.2.7.4.4.2 *Method Blanks (MB)*

For each MB analyzed in association with the reported samples, an Inorganic Analysis Data Sheet (CLP Form 1 or equivalent) must be included in the data package.

Multiple MB's (or multiple analyses of a single MB) shall be presented in chronological order for a given instrument with blank data for a second instrument, if applicable, following the data for the first instrument and so on.

#### 7.2.7.4.4.3 *Matrix Spike (MS)*

For each matrix spike analyzed in association with the reported samples, the following information must be included in the data package:

- 1) Inorganic Analysis Data Sheet (CLP Form 1 or equivalent)
  - a) Results for all spike and non-spike compound hits shall be reported as the numerical concentration value calculated from the raw data.
  - b) The field sample number recorded in the top right corner shall be comprised of the field sample number of the original sample used for the QC analyses, with a suffix of "S."

Note: The field sample number is the sample identifier found on the field chain of custody and not the number assigned by the laboratory.

#### 7.2.7.4.5 **Instrument Raw Data (Level 4 only)**

Copies of instrument run sequence raw data, arranged first by instrument type (in the following order: ICP, GFAA, CVAA) and second chronologically within instrument type raw data, are to be included in this section.

#### 7.2.7.4.6 **Screening Data**

If samples were screened (i.e., analyzed separately from and prior to the reported analysis data in order to determine the appropriate dilution factor), then the following information shall be provided at this point in the data package:

1. Screening results (e.g., LIMS generated report)
2. **(Level 4 only)** Raw data printout (integrator output, etc.) showing field sample number, instrument ID, date/time of analysis, lab filename, and analysis conditions;
3. Manual calculation of "X Factor", with analyst initials and date;

4. **(Level 4 only)** Raw data printout(s) for associated standard and blank analyses showing standard composition and concentration, instrument ID, date/time of analysis, and lab filename.

#### 7.2.7.4.7 Supporting Laboratory Records

Copies of the following laboratory documents must be provided in the data package:

1. Preparation Logs clearly identifying all reported samples (original and repeat preparations, where applicable);
2. Analysis Run Logs clearly identifying all reported samples (original and repeat analyses, where applicable);
3. Standard Preparation Logs including all working, secondary, and stock solutions used to support the reported analyses;
4. Internal chain of custody records, documenting the flow of each sample through the various laboratory departments during preparation, storage, and analysis;
5. Weigh logs (soil samples) indicating tare and final weights when taking the aliquot for analysis;
6. Percent moisture log (for solid samples) indicating tare, initial (tare plus solid aliquot), and final (tare plus solid aliquot after heating) weights;
7. Screening log clearly identifying all reported samples (original and repeat analyses, where applicable);

#### 7.2.7.5 *Miscellaneous Parameters*

Due to the variety of other analytical methods and techniques, defining the exact data to be reported to support the measurements for each of them is difficult. However, the general principles and philosophies described above for the other parameters can be used as a guide. In the case of anions (and perhaps cations) analyzed by ion chromatography, the types of data required for gas chromatography can be closely paralleled. For other, not so obvious correlations, the types of data to be included in the data package should include:

1. Preparation data to demonstrate that the samples were appropriately processed to observe the desired parameter;
2. Calibration data to demonstrate that the instrument was capable of consistent measurement during the course of analyses at all concentrations in the measurement range;
3. Calibration verification data to demonstrate that the laboratory calibration standards were accurately prepared;
4. Blank data to demonstrate that any positive results were not due to contamination introduced artificially from the time of sampling to the time of analysis;
5. Spike data to demonstrate that, if contamination were present, it could be detected accurately;
6. Duplicate data to demonstrate precision in the measurement process; and
7. Laboratory control sample data to demonstrate analytical system control.

Many of the forms used to report other parameters could be customized to report data for these parameters. Since many of the miscellaneous parameters may not be as automated as the previously discussed parameters, care must be taken to ensure that the raw data are clearly and legibly marked as to their significance.

#### **7.2.7.6    *Custody Records***

Copies of all chain of custody records for the reported samples must be included in the data package. Field chain of custody records will be presented first followed by internal chain of custody documents. The custody records in the data package must be legible and must contain laboratory receipt signatures, notations regarding sample condition on receipt at the laboratory, and cooler temperatures on receipt at the laboratory.

Documentation of the analyses requested for each sample must also be included in the package. If a separate “request for analysis” record is not included with the samples upon their arrival at the laboratory, then a copy of the client’s work request shall be included. If the requested analyses for each sample are clearly indicated on the chain of custody record, then no separate documentation is required.

**Table 7-1**  
**Typical Data Uses & Deliverable Levels**

<i>Examples of data uses</i>	<i>QC Level/Deliverables Format</i>	<i>Characteristics of data</i>
Site characterization Field Screening	Level 1	Qualitative or semiquantitative Indicator parameters
Site characterization Ongoing monitoring	Level 2	Semiquantitative or quantitative analysis Compound-specific General PARCCS assessment
Risk assessment Site characterization RIFS Closure	Level 3	Quantitative analysis Compound-specific Definitive PARCCS assessment
Risk assessment Site characterization RIFS Closure	Level 4	Quantitative analysis Compound-specific Definitive PARCCS assessment Defensible data validation

**Table 7-2**  
**Data Set Deliverables for Level 3<sup>1</sup> & Level 4 Reports**

<b>Method requirements</b>	<b>Deliverables</b>
<b>Requirements for all methods/parameters:</b>	
<ul style="list-style-type: none"> <li>Discussion of laboratory analysis, including any laboratory problems</li> </ul>	Case narratives
<b>Organics: GC/MS analysis</b>	
<b>Quality Control (QC) Summary</b>	
<ul style="list-style-type: none"> <li>Surrogate recoveries</li> </ul>	CLP <sup>2</sup> Form 2 or equivalent
<ul style="list-style-type: none"> <li>Matrix spike/spike duplicate data</li> </ul>	CLP Form 3 or equivalent
<ul style="list-style-type: none"> <li>Method blank data</li> </ul>	CLP Form 4 or equivalent
<ul style="list-style-type: none"> <li>GC/MS tune</li> </ul>	CLP Form 5 or equivalent
<ul style="list-style-type: none"> <li>GC/MS internal standard area data</li> </ul>	CLP Form 8 or equivalent
<b>Sample Data</b>	
<ul style="list-style-type: none"> <li>Sample results, including TICs (<i>Reconstructed ion chromatogram, quantitation report, mass spectra, NIST library searches</i>)</li> </ul>	CLP Form 1 or equivalent ( <i>Instrument generated raw data</i> )
<b>Standards Data</b>	
<ul style="list-style-type: none"> <li>GC/MS initial calibration data (<i>Reconstructed ion chromatogram, quantitation report</i>)</li> </ul>	CLP Form 6 or equivalent ( <i>Instrument generated raw data</i> )
<ul style="list-style-type: none"> <li>GC/MS continuing calibration data (<i>Reconstructed ion chromatogram, quantitation report</i>)</li> </ul>	CLP Form 7 or equivalent ( <i>Instrument generated raw data</i> )
<b>Raw Quality Control (QC) Data</b>	
<ul style="list-style-type: none"> <li><i>Tuning compound runs</i></li> </ul>	<i>Instrument generated raw data</i>
<ul style="list-style-type: none"> <li>Instrument blanks results</li> </ul>	CLP Form 1 or equivalent

**Table 7–2**  
**Data Set Deliverables for Level 3<sup>1</sup> & Level 4 Reports**

<b>Method requirements</b>	<b>Deliverables</b>
<i>(Reconstructed ion chromatogram, quantitation report, mass spectra, NIST library searches)</i>	<i>(Instrument generated raw data)</i>
<ul style="list-style-type: none"> <li>Method blanks results <i>(Reconstructed ion chromatogram, quantitation report, mass spectra, NIST library searches)</i></li> </ul>	CLP Form 1 or equivalent <i>(Instrument generated raw data)</i>
<ul style="list-style-type: none"> <li>Matrix spike/matrix spike duplicates (MS/MSD) results <i>(Reconstructed ion chromatogram, quantitation report)</i></li> </ul>	CLP Form 1 or equivalent <i>(Instrument generated raw data)</i>
<b>Screening data</b>	<b>Instrument generated raw data</b>
<b>Supporting laboratory records</b>	<b>Miscellaneous laboratory log book copies, etc.</b>
<b>GC analysis</b>	
<b>Quality Control (QC) Summary</b>	
<ul style="list-style-type: none"> <li>Surrogate recoveries</li> </ul>	CLP Form 2 or equivalent
<ul style="list-style-type: none"> <li>Matrix spike/spike duplicate data</li> </ul>	CLP Form 3 or equivalent
<ul style="list-style-type: none"> <li>Method blank data</li> </ul>	CLP Form 4 or equivalent
<b>Sample Data</b>	
<ul style="list-style-type: none"> <li>Sample results <i>(Gas chromatogram, quantitation report)</i></li> </ul>	CLP Form 1 or equivalent <i>(Instrument generated raw data)</i>
<b>Standards Data</b>	
<ul style="list-style-type: none"> <li>Initial calibration data of single component analytes</li> </ul>	CLP Form VI PEST-1 and PEST-2 or equivalent
<ul style="list-style-type: none"> <li>Initial calibration data of multicomponent analytes</li> </ul>	CLP Form VI PEST-3 or equivalent
<ul style="list-style-type: none"> <li>If calibration factors are used</li> </ul>	A form listing each analyte, the concentration of each standard, the relative calibration factor, the mean calibration factor, and the %RSD
<ul style="list-style-type: none"> <li>If a calibration curve is used</li> </ul>	Calibration curve and correlation coefficient
<ul style="list-style-type: none"> <li>Analyte resolution summary</li> </ul>	CLP Form VI PEST-4 or equivalent
<ul style="list-style-type: none"> <li>Performance evaluation mixture</li> </ul>	CLP Form VI PEST-5 or equivalent
<ul style="list-style-type: none"> <li>Individual standard mixture A</li> </ul>	CLP Form VI PEST-6 or equivalent
<ul style="list-style-type: none"> <li>Individual standard mixture B</li> </ul>	CLP Form VI PEST-7 or equivalent
<ul style="list-style-type: none"> <li>Calibration verification summary</li> </ul>	CLP Form VII PEST-1 or equivalent
<ul style="list-style-type: none"> <li>Calibration verification summary</li> </ul>	CLP Form VII PEST-2 or equivalent
<ul style="list-style-type: none"> <li>Analytical sequence and surrogate standard retention time summary</li> </ul>	CLP Form VIII PEST or equivalent
<ul style="list-style-type: none"> <li>Florisil cartridge check</li> </ul>	CLP Form IX PEST-1 or equivalent
<ul style="list-style-type: none"> <li>Pesticide GPC calibration</li> </ul>	CLP Form IX PEST-2 or equivalent
<ul style="list-style-type: none"> <li>Pesticide identification summary for single component analytes</li> </ul>	CLP Form X PEST-1 or equivalent
<ul style="list-style-type: none"> <li>Pesticide identification summary for multicomponent analytes</li> </ul>	CLP Form X PEST-2 or equivalent

**Table 7–2**  
**Data Set Deliverables for Level 3<sup>1</sup> & Level 4 Reports**

<b>Method requirements</b>	<b>Deliverables</b>
<ul style="list-style-type: none"> <li><i>Gas chromatograms and quantitation reports for all standards listed above</i></li> </ul>	<i>Instrument generated raw data</i>
<b>Raw Quality Control (QC) Data</b>	
<ul style="list-style-type: none"> <li>Instrument blanks results (<i>Gas chromatogram, quantitation report</i>)</li> </ul>	CLP Form 1 or equivalent ( <i>Instrument generated raw data</i> )
<ul style="list-style-type: none"> <li>Method blanks results (<i>Gas chromatogram, quantitation report</i>)</li> </ul>	CLP Form 1 or equivalent ( <i>Instrument generated raw data</i> )
<ul style="list-style-type: none"> <li>Matrix spike/matrix spike duplicates (MS/MSD) results (<i>Gas chromatogram, quantitation report</i>)</li> </ul>	CLP Form 1 or equivalent ( <i>Instrument generated raw data</i> )
<i>Screening data</i>	<i>Instrument generated raw data</i>
<i>Supporting laboratory records</i>	<i>Miscellaneous laboratory log book copies, etc.</i>
<b>Metals</b>	
<ul style="list-style-type: none"> <li>Sample results</li> </ul>	CLP Form 1 or equivalent
<ul style="list-style-type: none"> <li>Initial and continuing calibration standards, CRDL standard</li> </ul>	CLP Form 2 or equivalent, and dates of analyses and calibration curve, and the correlation coefficient factor
<ul style="list-style-type: none"> <li>Calibration and method blanks</li> </ul>	CLP Form 3 or equivalent and dates of analyses
<ul style="list-style-type: none"> <li>ICP interference check sample</li> </ul>	CLP Form 4 or equivalent
<ul style="list-style-type: none"> <li>Spike sample recovery</li> </ul>	CLP Form 5A or equivalent
<ul style="list-style-type: none"> <li>Postdigestion spike sample recovery for ICP metals</li> </ul>	CLP Form 5B or equivalent
<ul style="list-style-type: none"> <li>Postdigestion spike for GFAA</li> </ul>	CLP Form 5B or equivalent
<ul style="list-style-type: none"> <li>Duplicates</li> </ul>	CLP Form 6 or equivalent
<ul style="list-style-type: none"> <li>LCS</li> </ul>	CLP Form 7 or equivalent
<ul style="list-style-type: none"> <li>Method of standard additions</li> </ul>	CLP Form 8 or equivalent
<ul style="list-style-type: none"> <li>ICP serial dilution</li> </ul>	CLP Form 9 or equivalent
<ul style="list-style-type: none"> <li>Instrument detection limits</li> </ul>	CLP Form 10 or equivalent
<ul style="list-style-type: none"> <li>ICP linear range</li> </ul>	CLP Form 12 or equivalent
<ul style="list-style-type: none"> <li>Preparation log</li> </ul>	CLP Form 13 or equivalent
<ul style="list-style-type: none"> <li>Run log</li> </ul>	CLP Form 14 or equivalent
<b>Raw Data</b>	
<ul style="list-style-type: none"> <li><i>Instrument run sequence raw data, arranged first by instrument type (in the following order: ICP, GFAA, CVAA) and second chronologically within instrument type raw data</i></li> </ul>	<i>Instrument generated raw data</i>
<ul style="list-style-type: none"> <li><i>Supporting laboratory records</i></li> </ul>	<i>Miscellaneous laboratory log book copies, etc.</i>
<b>Wet Chemistry</b>	
<ul style="list-style-type: none"> <li>Sample results</li> </ul>	Report result (e.g., LIMS report)
<ul style="list-style-type: none"> <li>Matrix spike/duplicate spike</li> </ul>	Percent recovery (%R) and relative percent difference (RPD)
<ul style="list-style-type: none"> <li>Method blank</li> </ul>	Report result (e.g., LIMS report)

**Table 7–2**  
**Data Set Deliverables for Level 3<sup>1</sup> & Level 4 Reports**

<b>Method requirements</b>	<b>Deliverables</b>
• Initial calibration	Calibration curve and correlation coefficient
• Continuing calibration check	%R and percent difference (%D)
• Run log	Copy of run log
<b><i>Raw Data</i></b>	
<b><i>Instrument run sequence or manually created raw data, arranged alphabetically</i></b>	<b><i>Instrument or manually generated raw data</i></b>
<b><i>Supporting laboratory records</i></b>	<b><i>Miscellaneous laboratory log book copies, etc.</i></b>
Chain of Custody (COC)Records	Original copy of COCs forms
<sup>1</sup> Level 4 deliverables are identical to those specified for Level 3, except for the additional inclusion of all associated raw data; additional Level 4 raw data submittals are indicated in <b><i>bold, italicized</i></b> lettering.	
<sup>2</sup> Contract Laboratory Program (CLP) forms are based on the most current versions of the organic analysis (OLM0x.x) and inorganic analysis (ILM0x.x) series of CLP SOWs.	

## **8.0 *CORRECTIVE ACTIONS***

The Quality Assurance Program must include the mechanism for providing rapid corrective action in any problem area to minimize the possibility of producing data of questionable validity. These corrective actions are intended to eliminate both immediate problems involving sampling procedures, analytical procedures, improperly functioning instrumentation, or long-term problems involving systematic errors.

An effective corrective action consists of the following:

- Definition of the problem,
- Assignment of responsibility for implementing the corrective action,
- Investigation and determination of the cause of the problem,
- Determination of the corrective action to eliminate the problem,
- Determination of the effectiveness of the corrective action, and
- Documentation of the corrective action taken.

Critical to the success of project and/or laboratory corrective action initiatives is the application of a decision-tree process that results in consistent and defensible outcomes each time it is applied. The decision on whether to implement corrective actions must not be based on production constraints at the expense of meeting project DQOs that ultimately undermine data usability. When errors, deficiencies, or out-of-control excursions occur, the laboratory's QA program shall provide systematic procedures to resolve problems and restore proper functioning to the analytical system(s). Bench-level laboratory staff must be trained that corrective actions are necessary if: (1) matrix QC and laboratory control samples' data are outside the acceptable windows for precision and accuracy; (2) preparation or instrument calibration blanks exhibit analytes of interest or contaminants above acceptable levels; (3) outlier trends are observed in spike recoveries or RPD between duplicates; (4) there are unusual changes in method detection limits; (5) deficiencies are detected by the QA department during internal or external audits or from the results of PE samples; or (6) inquiries concerning data quality are received from a project manager. Corrective actions typically are initiated at the bench level by the analyst and/or peer reviewer, who reviews the sample preparation procedures for possible errors, checks the instrument calibration, spike, and calibration mixes, instrument sensitivity, and so on. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, Laboratory Project Manager, or QA Officer for further investigation. Submission of data by the laboratory that does not meet minimum project-specified DQOs can result in rejection of data or work being repeated at the contractor's expense.

The corrective action form presented in Figure 8-1 will be employed to document all corrective actions taken. Similar forms containing all of the specified information can be used by the laboratory. Corrective action forms may be initiated by any project individual who observes a major problem. All corrective actions require the approval signatures of the Project Manager and the Quality Assurance Officer. If more than one problem is involved, each problem and corrective action will be documented in a separate form.

## 8.1 Analytical Corrective Actions

***Standardized corrective action protocols play a significant role in the generation of analytical data of known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. This is of particular concern when the use of performed-based and/or hybrid methodology are employed in DNREC projects. Tables 8-1 and 8-2 summarize minimum requirements for performed-based method corrective actions protocols that must be used for data generated in conjunction DNREC analytical programs. The following major analytical method corrective actions or procedures are discussed in more detail and shall be required in the absence of project-specific requirements:***

### 8.1.1 Instrument Calibration

Sample analysis shall not be allowed until all initial calibrations and initial calibration verifications meet the appropriate requirements. All continuing calibration verifications that do not meet method requirements shall result in a review of the calibration, rerun of the appropriate calibration standard for the failed analytes, and, if necessary, reanalysis of all samples affected back to the previous acceptable continuing calibration verification check for the target analytes that failed. Continued failure of the CCV shall result in the construction of a new initial calibration curve followed by the reanalysis of all samples affected. If results are reported when calibration criterion has been exceeded, then all results reported shall be flagged.

### 8.1.2 Method QC

All method QC, including method blanks, laboratory control samples, matrix spikes, matrix duplicates, matrix spike duplicates, surrogate spikes, and other method specified QC, shall meet the appropriate project-specific requirements and associated corrective actions. In the absence of such criteria and/or actions, the corrective actions as described below shall be required. Failure of method QC shall result in the review of all affected data. If no errors can be noted, the affected sample(s) may need to be reanalyzed or reprep then reanalyzed within method holding times, if possible. If the situation is not corrected, and results reported, then the corresponding data shall be flagged. The Laboratory Project Manager shall be notified as soon as possible to discuss with DNREC personnel possible corrective actions should unusually difficult sample matrices be encountered.

#### 8.1.2.1 Method Blanks

The following criteria shall be used to evaluate the acceptability of the method blank data: The concentration of all method target analytes of interest shall be below the PQL concentration for each target analyte, or 10X less than the regulatory limit associated with that analyte, or 10X less

than the sample result for the same analyte, whichever is greater. The first step of corrective action is to assess the effect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action shall be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the method blank. The case narrative should also discuss the situation. If an analyte is found in the method blank and in some, or all, of the other batch samples at concentrations that are not greater than 10X above the amount present in the blank, then corrective action is required. The source of contamination shall be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant at concentrations less than 10X above the amount present in the blank, would be reanalyzed. If the contamination remains, the contaminated samples of the batch would be reprep and reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

#### **8.1.2.2    *Laboratory Control Samples***

The LCS is evaluated by comparing the recovery for all of the target analytes of interest to the recovery windows as determined by the laboratory or as specified in the project-specific DQOs. Laboratory generated control limits shall be reasonable for the performance-based methods. Windows that exceed reasonable limits would indicate the laboratory's implementation of that particular method is out of control and, therefore, unacceptable. When no project specific QC limits are identified, the laboratory's generated limits must be within the minimum recovery limits given in a published method similar in scope to the performance-based method employed by the laboratory for each target analyte of interest. A batch of samples shall be considered acceptable only for those analytes that had acceptable recoveries in the LCS. If target analytes of interest are outside the acceptance windows, corrective action is required. The first step of corrective action is to assess the effect on the samples. If an analyte in the LCS has a recovery above the upper acceptance window, but the same analyte is not detected in any of the other batch samples, no further corrective action shall be necessary. However, steps shall be taken to find the source of the problem and correct it. The case narrative should also discuss the situation. For all other situations, the LCS would be reanalyzed for the failed analytes only. If the second analysis fails, then the LCS, method blank, and all associated samples of the batch would be reprep and reanalyzed for the failed analytes only. When there are many analytes (e.g., >60 target analytes) the acceptance criteria may allow for the sporadic failure of one or two of the target analytes included within the LCS without requiring reanalysis.

#### **8.1.2.3    *Matrix Spike Samples***

The MS is evaluated by comparing the recovery for all target analytes of interest to the statistical process control (SPC) recovery windows as determined by the laboratory for samples of similar matrix, or as specified in the project-specific DQOs. MS data evaluation is more complex than method blank or LCS data evaluation since MSs measure matrix effects in addition to sample preparation and analysis errors. The heterogeneity of soil, grab samples, and sequentially collected water samples further complicates the evaluation since matrix specific accuracy assumes that the native concentrations in the duplicate analyses are constant. Concentrations of the target analytes in the sample can far exceed the spike amounts added. In general, laboratories will not base batch control on the results of the MS unless a general method failure is indicated or if sample cleanup appears to be necessary. MSs that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present.

#### 8.1.2.3.1 Parent Sample Concentration

If the native concentration of target analytes in the sample chosen for spiking is high relative to the spiking concentration, the differences in the native concentration between the unspiked sample and the spiked samples may contribute a significant error to the accuracy calculations making the accuracy measures unrepresentative of the true method and matrix performance. For this reason, if the native concentration is four or more times the spiked concentration, no further corrective action shall be necessary. It may be necessary to respike the sample at a higher level then reprep and reanalyze the sample based on project-specific requirements. If significant non-target interference exists, corrective action shall include the immediate notification of the Laboratory Project Manager to discuss with DNREC personnel possible courses of corrective action. These may include implementing additional cleanup procedures, method modifications, etc.

#### 8.1.2.3.2 Additional MS Issues

In all other situations, when a MS fails in accuracy for any spiked analyte, then corrective action would involve a review of the methods employed to determine their correctness and appropriateness. The use of alternative methods would be recommended after consulting with the DNREC personnel. These may include implementing additional cleanup procedures, method modifications, etc. The associated sample(s) shall be reprep then reanalyzed to verify the effect. The matrix effect would be confirmed if the repeated result is in the same direction and order of magnitude as the original results. If a general method failure was indicated, then the LCS, method blank, and all associated samples of the batch would be reprep and reanalyzed.

#### 8.1.2.4 *Sample Duplicate and Matrix Spike Duplicate Samples*

The MSD is evaluated using the same accuracy criteria as described for the MS. The sample duplicate (Dup) or MSD is evaluated by comparing the precision for all target analytes of interest to the SPC range limits as determined by the laboratory for samples of similar matrix, or as specified in the project-specific DQOs. These criteria should only be applied to concentrations of target analytes that are five times greater than each analyte's PQL. In general, laboratories will not base batch control on the results of the Dup or MSD unless a general method failure is indicated. Dups or MSDs that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. Corrective actions shall be performed as described for the MS.

#### 8.1.2.5 *Other Laboratory QC*

Listed below are examples of additional QC procedures and the appropriate corrective actions that would be required depending on the methods employed for a particular project. The failure of sample specific, not batch specific, QC would normally result in the affected sample(s) being reprep then reanalyzed.

##### 8.1.2.5.1 Surrogates

A surrogate is evaluated by comparing its recovery in each sample to the SPC windows as determined by the laboratory on samples of similar matrix or as specified in the project-specific DQOs. When no project specific QC limits are identified, the laboratory's generated surrogate recovery limits must be within the minimum recovery limits given in a published method similar in scope to the performance-based method employed by the laboratory. Surrogate spikes that

fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. This is demonstrated by re-extracting (if an extraction step is employed by the method) and/or reanalyzing the affected sample to reproducibly demonstrate matrix interference. If significant non-target interference occurs, corrective action shall include the immediate notification of the Laboratory Project Manager to discuss with DNREC personnel possible courses of corrective action. These may include implementing additional cleanup procedures, method modifications, etc. Surrogate failures in method blanks or laboratory control samples may be indicative of a general method failure and should be thoroughly investigated.

#### **8.1.2.5.2 Internal Standards**

An internal standard (IS) is evaluated by comparing its abundance to an acceptance range based on applying  $-50\%$  to  $+100\%$  factors to the IS abundance value obtained from the midpoint calibration standard from the initial calibration. Internal standard abundances in samples that fail to meet the  $-50\%/+100\%$  criteria would indicate that a potential matrix effect is present. This is demonstrated by reanalyzing the affected sample to reproducibly demonstrate matrix interference. Internal standard failures in method blanks or laboratory control samples may be indicative of a general method failure and should be thoroughly investigated.

## **8.2 Project-based Corrective Actions**

The following corrective actions or procedures shall be required in the absence of project-specific requirements:

### **8.2.1 Sample Login**

Discrepancies observed at time of sample receipt shall be documented on the Chain of Custody. The Laboratory Project Manager shall be contacted immediately for problem resolution.

### **8.2.2 Holding Times**

If samples and/or extracts/digestates/etc. cannot be prepared and/or analyzed within the method required holding times, the Laboratory Project Manager shall be immediately notified, such that an appropriate corrective action plan can be generated. If holding times are exceeded, and results reported, the resulting data shall be flagged.

### **8.2.3 Calculation Errors**

Reports shall be reissued if calculation and/or reporting errors are noted with any given data package. The case narrative shall clearly state the reason(s) for reissuance of the report.

### **8.2.4 On-site audits**

A corrective actions report shall be required that addresses any deficiencies noted during audits conducted by regulatory agencies during the time that the laboratory is actively processing samples associated with a DNREC project. If corrective actions are needed for major deficiencies that would affect data quality, the laboratory should notify DNREC personnel of other projects that may be affected.

**Table 8-1**  
**Performanced-based (Organic) Method Quality Control Acceptance Criteria**  
**and Corrective Action Requirements**

QC Application	QC Outcome								
	Absence of Contamination	Contamination Present (target cmpds. &/or TICs)	Acceptable Surrogate Recovery	Unacceptable Surrogate Recovery	Acceptable Recovery of Spiked Compounds	Unacceptable Recovery of Spiked Compounds	Acceptable RPD	Unacceptable RPD	Internal Standard Failure
Method Blank	<b>O</b>	<b>X<sub>1</sub></b>	<b>O</b>	<b>X<sub>2</sub></b>					<b>X<sub>14</sub></b>
Laboratory Control Sample			<b>O</b>	<b>X<sub>3</sub></b>	<b>O</b>	<b>X<sub>7</sub></b>			<b>X<sub>15</sub></b>
Laboratory Control Sample Duplicate			<b>O</b>	<b>X<sub>3'</sub></b>	<b>O</b>	<b>X<sub>8</sub></b>	<b>O</b>	<b>X<sub>11</sub></b>	<b>X<sub>15</sub></b>
Matrix Spike			<b>O</b>	<b>X<sub>4</sub></b>	<b>O</b>	<b>X<sub>9</sub></b>			<b>X<sub>16</sub></b>
Matrix Spike Duplicate			<b>O</b>	<b>X<sub>4'</sub></b>	<b>O</b>	<b>X<sub>10</sub></b>	<b>O</b>	<b>X<sub>12</sub></b>	<b>X<sub>16</sub></b>
Sample Duplicate			<b>O</b>	<b>X<sub>5</sub></b>			<b>O</b>	<b>X<sub>13</sub></b>	<b>X<sub>16</sub></b>
Reportable Sample			<b>O</b>	<b>X<sub>6</sub></b>					<b>X<sub>16</sub></b>

- O** - passes specification, report associated samples in QC batch.
- X<sub>1</sub>** - Concentration of contaminant (x): (1)  $x < \text{MDL}$ , report samples unqualified; (2)  $\text{MDL} < x < \text{PQL}$ , report samples with same contaminant with B flag; (3)  $x > \text{PQL}$ , reanalyze samples (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) if same contaminant is found in samples at levels discussed in the bullet items below; if samples do not contain blank contaminant report results unqualified (narrate contaminated blank if necessary). In cases where

associated samples contain the same contaminant found in the method blank use the following criteria to establish data usability:

- **If the sample contains the contaminant at levels of at least 10 times that in the blank**, then the likely contribution to the sample from the contaminant in the laboratory environment is at most 10 %. Since most of the methods in question are no more accurate than that level the possible contamination is negligible.
- **If the sample contains the contaminant at levels of at least 5 times but less than 10 times the blank result**, the compound is probably present in the sample, but the numerical result should be considered an upper limit of the true concentration (narrative should indicate the positive bias of the results).
- **If the sample contains the contaminant at levels below 5 times the level in the blank**, there is no adequate means by which to judge whether or not the sample result is attributable to laboratory contamination. The results for that compound in that sample are unacceptable and the sample must be reanalyzed (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed).  
Note: In applying the above concentration level rules, when a sample undergoes dilution the contaminant concentration found in the blank must be multiplied by the dilution factor applied to the sample before determining whether the concentration found in the sample is above the 5X & 10X decision levels.

- X<sub>2</sub>** - reanalyze (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) all samples in QC batch (Special exception: if samples exhibit acceptable surrogate recovery and contain no reportable targeted compounds, OK to report samples with narrative discussion on blank surrogate failure).
- X<sub>3</sub>** - reanalyze (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) all samples in QC batch (Special exceptions: 1) if LCS Dup was analyzed and exhibited acceptable surrogate recoveries, report samples unqualified with narrative explanation of random laboratory error or 2) if the spiked targeted compounds in LCS recover within acceptance limits then the system can be judged to be in control and the surrogate standard failure can be attributed to random laboratory error and addressed in the report narrative).
- X<sub>3</sub>** - see special exception note in **X<sub>3</sub>**.
- X<sub>4</sub>** - 1) if unspiked parent sample exhibited similar surrogate failure, report results unqualified and narrate matrix effect on surrogate recovery; 2) reanalyze (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) all samples in QC batch (Special exception: if spiked target compounds recovered acceptably in matrix spike, report samples unqualified with narrative explanation OR if MSD was analyzed and exhibited acceptable surrogate recoveries, report samples unqualified with narrative explanation (e.g., random laboratory error).
- X<sub>4</sub>** - 1) see 1) from **X<sub>4</sub>** above; 2) see special note in **X<sub>4</sub>** 2) above.
- X<sub>5</sub>** - 1) if parent sample exhibited similar surrogate failure, report results unqualified and narrate matrix effect on surrogate recovery; 2) reanalyze sample (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed); if reanalysis has acceptable surrogates, report only reanalysis results.
- X<sub>6</sub>** - reanalyze sample (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed), if reanalysis has; 1) similar surrogate failure report first

analysis and narrate matrix effect on surrogate recovery; OR 2) exhibits acceptable surrogate recovery report only reanalysis sample results.

- X<sub>7</sub>** - reanalyze (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) all samples in QC batch unless one or more of the following special exceptions applies: 1) if LCSDup was analyzed and exhibited acceptable recoveries for the compounds which failed in the LCS, report sample results unqualified and narrate LCS failure issue as random laboratory error; OR 2) if LCSDup was not analyzed and the matrix spike exhibited acceptable recoveries for the compound(s) which failed in the LCS, then the MS becomes the controlling measurement to demonstrate that the system was under control, results can be reported unqualified and the LCS failure should be narrated as random laboratory error; OR if neither 1) or 2) are applicable, 3) data rejection or usability in cases where LCS recovery criteria have not been met can be established based upon the following guidelines:
- If the concentration of the **LCS is above acceptance limits but the analyte is not detected in an associated sample**, then it is unlikely that the sample result is affected by the failure and the sample result can be reported unqualified.
  - If the concentration of the **LCS is above acceptance limits and that analyte is detected in the sample**, then the numerical sample result may represent an upper limit of the true concentration, and the end data user should be informed of the potential positive bias in the report narrative.
  - If the concentration of the **LCS is below acceptance limits but that analyte is detected in an associated sample**, then the sample result may represent the lower limit of the true concentration for that analyte, and the end user should be informed of the potential negative bias in the report narrative.
  - If the concentration of the **LCS is below acceptance limits and that analyte is not detected in an associated sample**, then the sample data are suspect and cannot be considered valid for regulatory compliance purposes (i.e., associated samples must be re-extracted and/or reanalyzed).
- X<sub>8</sub>** - see special exception 1) in **X<sub>7</sub>** above.
- X<sub>9</sub>** - qualify results as matrix interference (Note: if MSD was analyzed, the compounds which failed in the MS must also have failed in the MSD in order to substantiate matrix interference) according to the following guidelines:
- If the recovery of the **MS is above acceptance limits but the analyte is not detected in an associated sample**, then it is unlikely that the sample result is affected by the failure and the sample result can be reported unqualified.
  - If the recovery of the **MS is above acceptance limits and that analyte is detected in the sample**, then the numerical sample result may represent an upper limit of the true concentration, and the end data user should be informed of the potential positive bias in the report narrative.
  - If the recovery of the **MS is below acceptance limits but that analyte is detected in an associated sample**, then the sample result may represent the lower limit of the true concentration for that analyte, and the end user should be informed of the potential negative bias in the report narrative.
  - If the recovery of the **MS is below acceptance limits and that analyte is not detected in an associated sample**, then the sample data are suspect and cannot be

considered valid for regulatory compliance purposes (i.e., associated samples must be re-extracted and/or reanalyzed).

- X<sub>10</sub>** - same as **X<sub>9</sub>** above.
- X<sub>11</sub>** - if either the LCS or LCSDup passes acceptance criteria for the analytes which failed in the other, report sample results unqualified and narrate the LCS failure issue as random laboratory error. If both LCS samples experience unacceptable recoveries for analytes of interest and the associated analyte RPD specifications are also not achieved, then reanalyze (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed) all associated samples in the QC batch. [Special exception: if an assignable cause, which is independent from the analytical system which would also adversely impact samples in the QC batch, can be verified for the LCS failures (e.g., spiking error in preparing LCS samples), the QC batch can be accepted if the associated MS/MSD sample recoveries and RPDs meet the LCS acceptance criteria.
- X<sub>12</sub>** - review sample appearance to assess homogeneity; if RPD failure can not be attributed to sample nonhomogeneity, report sample results unqualified and narrate the MS (or MSD) failure issue as random laboratory error.
- X<sub>13</sub>** - review sample appearance to assess homogeneity; if failure can not be attributed to sample nonhomogeneity, reanalyze sample duplicate (if sample preparation includes an extraction step, the sample must be re-extracted and reanalyzed).
- X<sub>14</sub>** - reanalyze blank; if IS fail again, reanalyze (if sample preparation includes an extraction step, the samples must be re-extracted and reanalyzed) all samples in QC batch (Special exception: if samples exhibit acceptable IS results and contain no reportable targeted compounds, OK to report samples with narrative discussion on blank IS failure).
- X<sub>15</sub>** - reanalyze LCS; if IS fail again, reanalyze (if sample preparation includes an extraction step, the samples must be re-extracted and reanalyzed) all samples in QC batch (Special exception: if LCSDup was analyzed and exhibited acceptable IS, report samples unqualified with narrative explanation of random laboratory error in LCS IS failure.)
- X<sub>16</sub>** - reanalyze sample or sample extract (re-extraction of sample is not required) to reproducibly demonstrate that matrix interference caused IS failure; if reanalysis passes IS criteria, report reanalysis. Note: if parent sample of MS/MSD/DUP exhibits IS failure and the indicated matrix QC sample also shows IS failure, no further reanalyses are required. Narrate all cases of matrix-related IS failures.

References:

*Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring*, USEPA Office of Water, EPA 821-B-93-001, June 1993.  
*Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures*, USEPA Office of Emergency and Remedial Response, EPA/540/G-90/004 Interim Final, April 1990.  
*USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, USEPA Office of Solid Waste and Emergency Response, EPA540/R-94/012, February 1994.

Table 8-2

Performanced-based (Inorganic) Method Quality Control Acceptance Criteria  
and Corrective Action Requirements

QC Application	QC Outcome					
	Absence of Contamination	Contamination Present (target cmpd &/or matrix interference)	Acceptable Recovery of Spiked Compounds	Unacceptable Recovery of Spiked Compounds	Acceptable RPD	Unacceptable RPD
Method Blank	<b>O</b>	<b>X<sub>1</sub></b>				
Laboratory Control Sample			<b>O</b>	<b>X<sub>2</sub></b>		
Laboratory Control Sample Duplicate			<b>O</b>	<b>X<sub>3</sub></b>	<b>O</b>	<b>X<sub>6</sub></b>
Matrix Spike			<b>O</b>	<b>X<sub>4</sub></b>		
Matrix Spike Duplicate			<b>O</b>	<b>X<sub>5</sub></b>	<b>O</b>	<b>X<sub>7</sub></b>
Sample Duplicate					<b>O</b>	<b>X<sub>8</sub></b>
Reportable Sample	<b>O</b>	see qualifications below for guidance	<b>O</b>	see qualifications below for guidance	<b>O</b>	see qualifications below for guidance

- O** - passes specification, report associated samples in QC batch.
- X<sub>1</sub>** - Concentration of contaminant (x): (1)  $x < \text{MDL}$ , report samples unqualified; (2)  $\text{MDL} < x < \text{PQL}$ , report samples with same contaminant with B flag; (3)  $x > \text{PQL}$ , reanalyze samples (if sample preparation includes an extraction/digestion step, the sample must be re-extracted/redigested and reanalyzed) if same contaminant is found in samples at levels discussed in the bullet items below; if samples do not contain blank contaminant report results unqualified (narrate contaminated blank if necessary). In cases where associated samples contain the same contaminant found in the method blank use the following criteria to establish data usability:

- **If the sample contains the contaminant at levels of at least 10 times that in the blank**, then the likely contribution to the sample from the contaminant in the laboratory environment is at most 10 %. Since most of the methods in question are no more accurate than that level the possible contamination is negligible.
- **If the sample contains the contaminant at levels of at least 5 times but less than 10 times the blank result**, the compound is probably present in the sample, but the numerical result should be considered an upper limit of the true concentration (narrative should indicate the positive bias of the results).
- **If the sample contains the contaminant at levels below 5 times the level in the blank**, there is no adequate means by which to judge whether or not the sample result is attributable to laboratory contamination. The results for that compound in that sample are unacceptable and the sample must be reanalyzed (if sample preparation includes an extraction/digestion step, the sample must be re-extracted/redigested and reanalyzed).

Note: In applying the above concentration level rules, when a sample undergoes dilution the contaminant concentration found in the blank must be multiplied by the dilution factor applied to the sample before determining whether the concentration found in the sample is above the 5X & 10X decision levels.

X<sub>2</sub> - reanalyze (if sample preparation includes an extraction/digestion step, the sample must be re-extracted/redigested and reanalyzed) all samples in QC batch unless one or more of the following special exceptions applies: 1) if LCSDup was analyzed and exhibited acceptable recoveries for the compounds which failed in the LCS, report sample results unqualified and narrate LCS failure issue as random laboratory error; OR 2) if LCSDup was not analyzed and the matrix spike exhibited acceptable recoveries for the compound(s) which failed in the LCS, then the MS becomes the controlling measurement to demonstrate that the system was under control, results can be reported unqualified and the LCS failure should be narrated as random laboratory error; OR if neither 1) or 2) are applicable, 3) data rejection or usability in cases where LCS recovery criteria have not been met can be established based upon the following guidelines:

- If the concentration of the **LCS is above acceptance limits but the analyte is not detected in an associated sample**, then it is unlikely that the sample result is affected by the failure and the sample result can be reported unqualified.
- If the concentration of the **LCS is above acceptance limits and that analyte is detected in the sample**, then the numerical sample result may represent an upper limit of the true concentration, and the end data user should be informed of the potential positive bias in the report narrative.
- If the concentration of the **LCS is below acceptance limits but that analyte is detected in an associated sample**, then the sample result may represent the lower limit of the true concentration for that analyte, and the end user should be informed of the potential negative bias in the report narrative.
- If the concentration of the **LCS is below acceptance limits and that analyte is not detected in an associated sample**, then the sample data are suspect and cannot be considered valid for regulatory compliance purposes (i.e., associated samples must be re-extracted/redigested and/or reanalyzed).

**X<sub>3</sub>** - see special exception 1) in **X<sub>2</sub>** above.

- X<sub>4</sub>** - if the native concentration of the analyte of interest does not exceed the spike added concentration by a factor of 4X, qualify results as matrix interference (Note: if MSD was analyzed, the compounds which failed in the MS must also have failed in the MSD in order to substantiate matrix interference) according to the following guidelines:
- If the recovery of the **MS is above acceptance limits but the analyte is not detected in an associated sample**, then it is unlikely that the sample result is affected by the failure and the sample result can be reported unqualified.
  - If the recovery of the **MS is above acceptance limits and that analyte is detected in the sample**, then the numerical sample result may represent an upper limit of the true concentration, and the end data user should be informed of the potential positive bias in the report narrative.
  - If the recovery of the **MS is below acceptance limits but that analyte is detected in an associated sample**, then the sample result may represent the lower limit of the true concentration for that analyte, and the end user should be informed of the potential negative bias in the report narrative.
  - If the recovery of the **MS is below acceptance limits and that analyte is not detected in an associated sample**, then the sample data are suspect and cannot be considered valid for regulatory compliance purposes (i.e., associated samples must be re-extracted/redigested and/or reanalyzed).

If the native concentration exceeds the spike added concentration by a factor of 4X then the statistical evaluation for percent recovery is deemed not applicable.

**X<sub>5</sub>** - same as **X<sub>4</sub>** above.

- X<sub>6</sub>** - if either the LCS or LCSDup passes acceptance criteria for the analytes which failed in the other, report sample results unqualified and narrate the LCS failure issue as random laboratory error. If both LCS samples experience unacceptable recoveries for analytes of interest and the associated analyte RPD specifications are also not achieved, then reanalyze (if sample preparation includes an extraction/digestion step, the sample must be re-extracted/redigested and reanalyzed) all associated samples in the QC batch. [Special exception: if an assignable cause, which is independent from the analytical system which would also adversely impact samples in the QC batch, can be verified for the LCS failures (e.g., spiking error in preparing LCS samples), the QC batch can be accepted if the associated MS/MSD sample recoveries and RPDs meet the LCS acceptance criteria.

**X<sub>7</sub>** - review sample appearance to assess homogeneity; if RPD failure can not be attributed to sample nonhomogeneity, report sample results unqualified and narrate the MS(or MSD) failure issue as random laboratory error.

- X<sub>8</sub>** - if the native concentration is a factor of at least 5X above the PQL, review sample appearance to assess homogeneity; if failure can not be attributed to sample nonhomogeneity, reanalyze sample duplicate (if sample preparation includes an extraction/digestion step, the sample must be re-extracted/redigested and reanalyzed). If the native concentration is less than 5X greater than the PQL, then the statistical evaluation for precision is deemed not applicable.

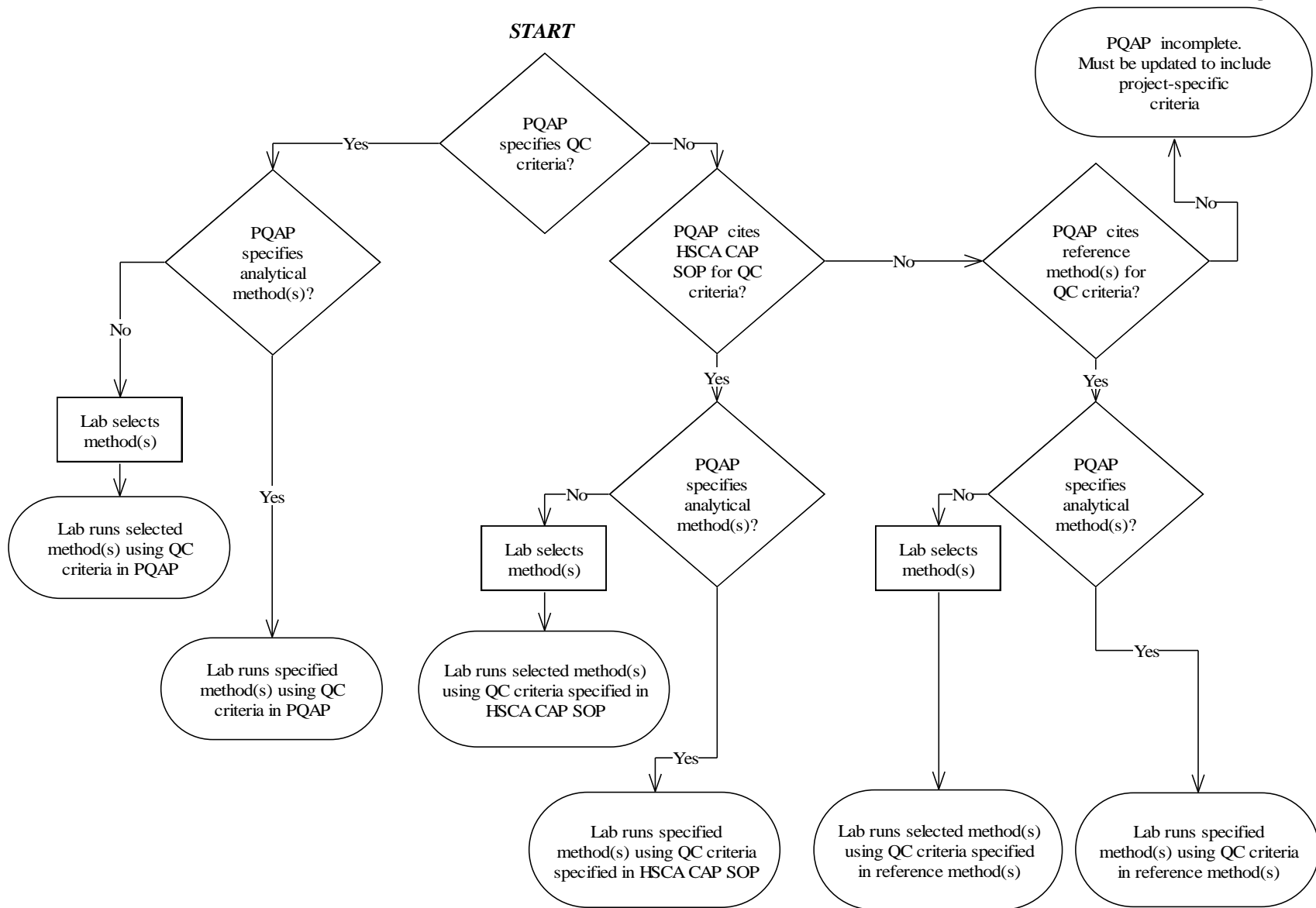
References:

*Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring*, USEPA Office of Water, EPA 821-B-93-001, June 1993.

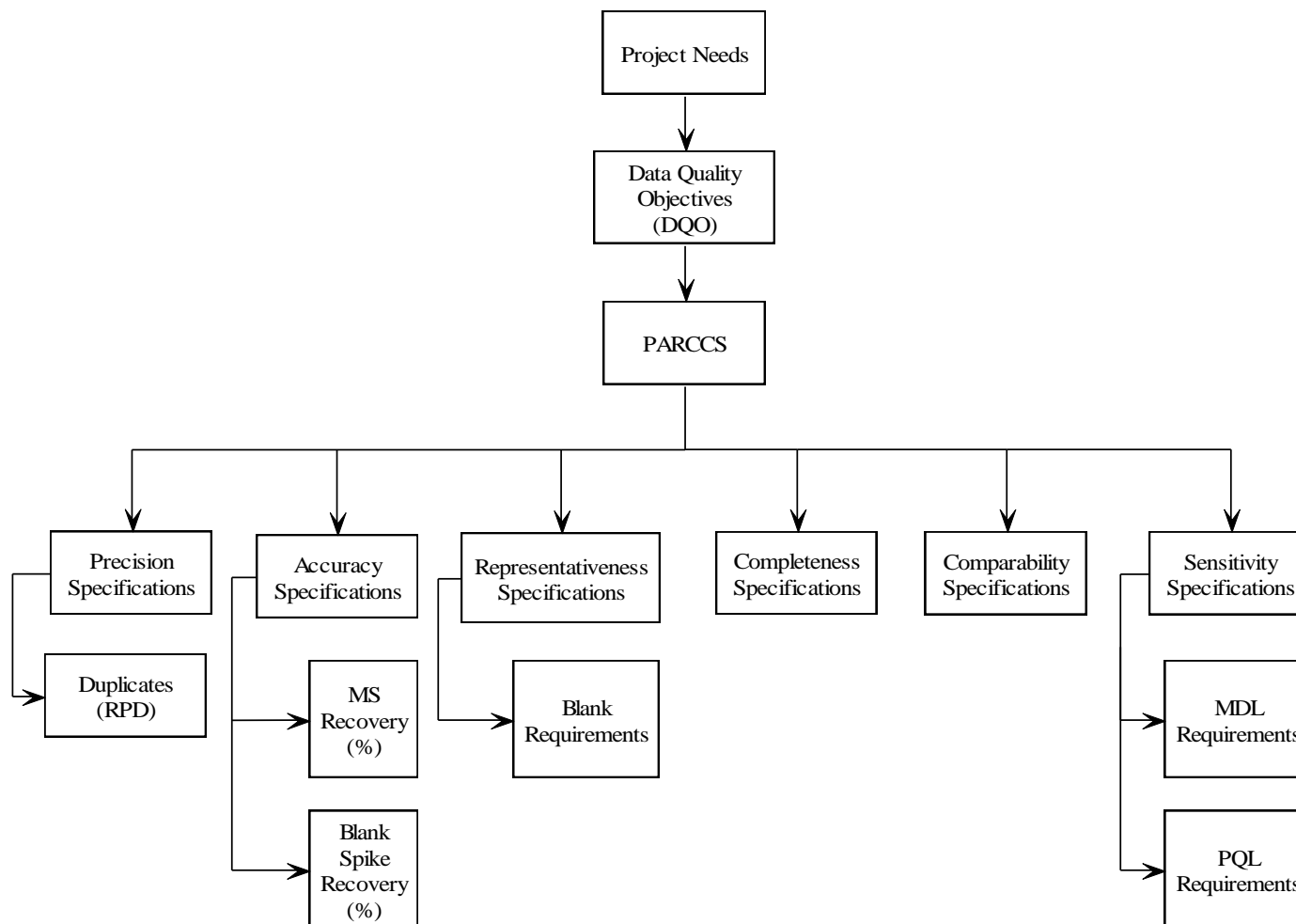
*Guidance on the Documentation and Evaluation of Trace Metal Data Collected for Clean Water Act Compliance Monitoring*, USEPA Office of Water Engineering and Analysis Division (4303), EPA 821-B-95-002, April 1995.

*Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures*, USEPA Office of Emergency and Remedial Response, EPA/540/G-90/004 Interim Final, April 1990.

*USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*, USEPA Office of Solid Waste and Emergency Response, EPA-540/R-94-013, February 1994.



**Figure 1.1 Hierarchy for selection of analytical methods and performance criteria under DNREC performance based method system.**



**Figure 1 Relationship Between Project Needs, Data Quality Objectives and Analytical QC Specifications, with Typical QC Measurements**

**Figure 8-1**

QUALITY ASSURANCE  
CORRECTIVE ACTION REQUEST FORM

Originator \_\_\_\_\_ Date \_\_\_\_\_

Nature of Problem \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Recommended Corrective Action \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Reviewed by \_\_\_\_\_ Date \_\_\_\_\_

Action Assigned to \_\_\_\_\_ Date Due \_\_\_\_\_

Action Completed \_\_\_\_\_ Date \_\_\_\_\_

(Attach Description of Solution) Signed

Reviewed by \_\_\_\_\_ Date \_\_\_\_\_

Signature Project Manager

Reviewed by \_\_\_\_\_ Date \_\_\_\_\_

Signature - QA Officer

## ***9.0 Laboratory Data Review***

All data generated by the laboratory for DNREC projects must undergo documented reviews, as established in written laboratory procedures and guidelines. The procedures must define all aspects of data review, including data reduction, validation and reporting. The purpose of the analytical data review process is to ensure through an extensive internal assessment performed prior to report release that the data are both valid and authentic for their intended use by DNREC.

The following elements should be considered when developing documented laboratory data review requirements:

- percentage of data to be reviewed and level of review to be applied;
- type of data to be reviewed (e.g., final results, raw data, calculations);
- verification that reported results, existing raw data, and related QC information (e.g., blanks, spikes, duplicates) conform to prescribed sensitivity, accuracy, precision, and any other criteria established to meet project objectives;
- verification that instrument conditions (e.g., tunes, initial and continuing calibrations, response factors, correlation coefficients) conform to prescribed standards established in regulatory-based and/or performance-based methods;
- type(s) of review (e.g., analyst, analytical peer, supervisor, lab management, QA function);
- confirmation that results are representative of the sample received;
- confirmation of analytical consistency and completeness;
- confirmation of data package consistency and completeness; and
- verification that the data reported are authentic and of traceable integrity.

### **9.1 Data Review Process**

At a minimum, all data must be initially reviewed by the analyst responsible for its generation, peer reviewed, reviewed by a technical supervisor, and approved for release by management. In addition, at least 10% of DNREC project-derived data for each analytical method must undergo a QA review. Each step of the review process must be documented with the initials and date of review by the assigned reviewer.

#### **9.1.1 Analyst Review**

Each analyst is responsible to review the quality of their work based on the laboratory established set of procedures and guidelines. The purpose of this review is to ensure that the data comply with method and project-specific requirements, and that any aspects of noncompliance are documented in the raw data and/or associated project file. This review step must encompass, when applicable, the following minimum verification elements:

- holding times met;
- accuracy and completeness of sample preparation information;

- accuracy and completeness of analysis information;
- adherence to appropriate SOPs;
- accuracy and completeness of analytical results;
- correct interpretation of raw data, including all spectra and manual integrations;
- evaluation of QC results relative to established control limits and outliers appropriately addressed; and
- completeness of documentation (e.g., nonconformance issues noted in appropriate documentation, etc.).

### **9.1.2 Peer Review**

The peer review step must be completed by an analyst that is qualified to perform the analytical method under which the subject data was generated. The review must also be conducted according to the laboratory established procedures and must encompass 100% of the data generated for the analytical method. This review step must encompass, when applicable, the following minimum verification elements:

- check 100% of manual entries for transcription errors and spot check automated data uploads for accuracy;
- check 100% of manual calculations for accuracy;
- check reported values of dilutions;
- spot checks of computer calculations to verify program validity;
- check for compliance with method and project-specific QC requirements;
- check for completeness of raw data or supporting documentation (e.g., preparation logbooks, extraction bench sheets, etc.);
- confirm spectral interpretations and appropriateness of manual integrations;
- check descriptions of nonconformances and anomalies; and
- evaluate overall reasonableness of results.

### **9.1.3 Technical Review**

The technical review step must be completed by a supervisor or data review specialist qualified to evaluate data generated by the referenced analytical method. The review must also be conducted according to the laboratory established procedures and must encompass 100% of the data generated for the analytical method. This review step must encompass, when applicable, the following minimum verification elements:

- confirmation that appropriate laboratory SOPs and project-specific requirements are met;
- accuracy and compliance of calibration data;
- QC samples/indicators are within established acceptance limits and outliers appropriately addressed;
- qualitative identification of sample components is correct;
- quantitative results, and any associated qualifier flags, are correct;
- raw data, including spectra and manual integrations, have been correctly interpreted; and
- documentation is complete and authentic.

#### **9.1.4 Management Review**

The management review step is to be completed by the laboratory DNREC project manager, laboratory manager or qualified management designee authorized to release data. The scope and content of the management review can be established by the laboratory; however, it must provide a total assessment overview of the data package, including sample receipt, to ensure consistency and compliance with the DNREC project-specific requirements. Authority to release data following the management review must be documented in the laboratory QA plan or project-specific QAPP.

#### **9.1.5 QA Review**

The QA review is performed by the laboratory QA Officer or qualified QA department personnel. Reviews of data from each laboratory section must be conducted on a routine basis; however, this review is not part of the normal production data review process. At least 10% of data generated using each analytical method employed for DNREC projects must be reviewed by a member of the QA staff. The QA reviews can be performed using procedures developed for the technical and management reviews discussed previously on DNREC data packages randomly selected. The overall purpose of the QA review is to verify the following:

- compliance with required QC practices;
- compliance with approved SOPs; and
- compliance with method and DNREC project requirements.

Nonconformance reports are required for any errors noted and corrective actions implemented to prevent repeat nonconformances.

### **9.2 Data Validation**

Data validation refers to the third party review process of the analytical data supplied by the laboratory. This review is a comprehensive assessment of the raw data to determine if the results are usable and if any qualifiers are needed. Full data packages, as defined within the HSCA SOPCAP, must be supplied for proper data validation.

DNREC will conduct data validation for Preliminary Assessment and Site Investigation (PA/SI) programs because this level of quality assurance must be maintained in accordance with United States Environmental Protection Agency (US EPA) procedures and policies.

In addition, DNREC will conduct data validation from Delaware orphan or enforcement sites that may require future litigation under HSCA or any other DNREC environmental program.

All data performed under the HSCA SOPCAP must undergo data validation using the US EPA National Functional Guidelines for data review with the following exceptions:

Analytical data from DNREC sites that have a Brownfields Development Agreement (BDA) or VCP agreement will not routinely require data validation as long as the analysis is performed by a HSCA approved laboratory. In addition, analytical data from Phase I or Phase II Environmental Site Assessments (ESAs) that are not under DNREC oversight and are performed by a HSCA approved consultant for use as Facility Evaluations (FE) will not require data validation

providing the HSCA approved laboratory is utilized. DNREC maintains oversight of the laboratory approval process as well as a list of approved labs. DNREC, at its discretion, may determine that site-specific data validation is warranted and will communicate this need to the appropriate parties.

Although data validation will not be routinely required for Brownfields or VCP sites, it is essential that each data report be reviewed for accuracy and completeness. This includes the following items:

All Tentatively Identified Compounds (TICS) must be evaluated for potential impact on the site assessment and their effect on any potential remediation.

Analysis results should be compared to any past data results and any available screen data to insure precision and accuracy. A direct comparison of field screening data and the fixed laboratory data must be included in all reports. Any inconsistencies must be investigated. This investigation will include a confirmation of the analytical results from the fixed laboratory.

Any non-conformance issue reported by the laboratory will be reviewed for potential impact on the data.

For a comprehensive evaluation of the analytical chemistry data, please refer to section 9.1 to insure all pertinent information has been provided by the laboratory.

## **Appendix A Examples of Laboratory Forms**

RSK02035.doc